

Use of Amine Oxide Surfactants for Chemical Flooding EOR

Topical Report  
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November 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

Prepared for  
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By David K. Olsen

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## ABSTRACT

The use of amine oxides with and without alcohols as cosolvents, and in combination with other surfactants as mixed micellar formulations for enhanced oil recovery by surfactant flooding was investigated. Amine oxides are a salt-tolerant class of surfactants that produce low interfacial tension and can develop viscosity without the addition of polymers. These salt-tolerant formulations generate three-phase regions with hydrocarbons over a broad salinity range, develop moderate solubilization, and produce low interfacial tensions, however oil recovery from amine oxide-alcohol phase behavior optimized formulations was directly dependent upon the quantity of surfactant injected. The large pore volume and high concentration of surfactant required prohibits their economic use as the primary surfactant in chemical flooding EOR. Dimethylalkylamine oxides are useful as cosurfactants and viscosifiers in formulations with other surfactants for chemical flooding EOR but the use of ethoxylated and propoxylated amine oxides should be avoided due to the decomposition of these amine oxides under reservoir conditions. Phase behavior, phase inversion temperatures, and viscosity scans have been correlated with surfactant structures to provide a guide for amine oxide applications in chemical flooding.

## EXECUTIVE SUMMARY

Research on amine oxides as primary surfactants should be suspended as they require too much surfactant to compete with synthetic sulfonates in chemical EOR for oil recovery. Amine oxides, especially dimethylalkylamine oxides where the alkyl group that is longer than tetradecyl, could be used as cosurfactants with water soluble sulfonates of approximately the same salinity tolerance to formulate chemical flooding systems that develop low interfacial tension and viscosity in the surfactant slug without polymer addition. The use of ethoxylated or propoxylated amine oxides in the same systems should be avoided due to decomposition of these amine oxide under reservoir conditions.

## INTRODUCTION

The use of surfactants in enhanced oil recovery (EOR) in either low-tension, low-concentration waterflooding or in micellar-polymer flooding has been pursued for the past two decades with mixed success. However, chemical flooding has yet to be proven to be economical on a commercial scale. Within the past 5 years, depressed oil prices have curtailed most industrial research on surfactant flooding. Reviews of progress in chemical flooding technology have indicated that problems that impede development of this technology include: difficulties in designing and optimizing chemical formulations in laboratories, the major step of taking an optimized chemical process from a well characterized and

controlled laboratory environment to the field, and selection of cost-effective surfactants.<sup>1-6</sup> Applications of chemical flooding in reservoirs have been determined to be far more complicated than originally envisioned, and although great progress has been made<sup>7-8</sup> and several technically successful pilot tests have been completed,<sup>7</sup> major challenges<sup>4-6</sup> must be resolved before chemical flooding can be widely applied. A high front-end expenditure for surfactant severely impacts the economics of the process and limits its commercial application.<sup>9</sup> This work addressed cost-effective surfactants by investigating a class of surfactant that has received little attention but has potential for chemical flooding by providing viscosity to surfactant slugs.

## BACKGROUND

Reservoirs that have performed well under waterflooding are the primary targets for chemical flooding.<sup>3,10</sup> The major factors that influence the amount of oil recovered by EOR include the oil saturation, the relative mobility of the reservoir oil and injected fluid, the wettability characteristics of rock surfaces in the reservoir and the interfacial tension between the injected fluid and the reservoir oil. Obviously, if plug-type flow of oil can be achieved by the displacing fluid, substantial amounts of oil in place could be displaced. However, this is not always accomplished because of reservoir heterogeneity and because most displacing fluids travel faster through the more permeable zones and injected fluids often have an adverse mobility ratio. Such unfavorable conditions result in bypassing significant quantities of oil which leads to low oil recovery and early abandonment of oil fields. Liquids have a more favorable mobility ratio than gases in displacing crude oil primarily because of their greater viscosity. To improve on these factors, the use of larger pore volumes of viscosified (addition of polymers) surfactant (for reduction in interfacial tension) have been pursued in chemical flooding and profile modification methods to help block high-permeability streaks and maintain the effectiveness of optimized surfactant slugs.

A review of the history of oil production technology indicates that many of the problems encountered with reservoirs that were amenable to chemical flooding were caused by inadequate reservoir management. Air injection was a common practice in the United States in the 1930s through the late 1940s and was replaced by waterflooding in the late 1940s and early 1950s, which resulted in significantly better oil recovery. However, the mobility ratio between water and most crude oils is usually unfavorable. Numerous modifications have been employed to overcome this problem including thickening water with various materials such as polymers (both polyacrylamides and biopolymers), or foams, or emulsions (viscous water-oil emulsions). Polymer floods have been successful in accelerating the production of oil but rarely have they reduced the oil saturation below that expected from waterflooding. Operators frequently flooded reservoirs with waters of compositions that were intended to be chemically compatible but were of quite different composition from that of the connate brines in their

fields. This practice resulted in wide salinity contrasts between areas that had been waterflooded and those areas of lower permeability and higher oil saturation that had not been swept but are target areas for a chemical flood with good mobility control. Thus, the conditions of candidate reservoirs for chemical flooding are often the result of both nature and man's manipulations.

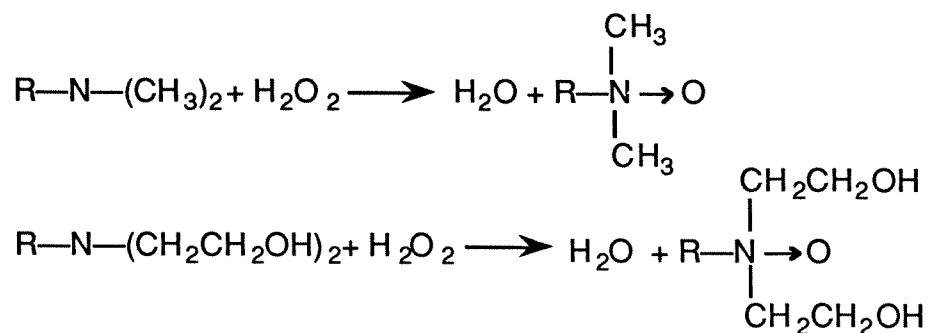
The design of a surfactant flooding system must not only be optimized in the laboratory but also have the flexibility to accommodate the variations in conditions that occur in the reservoir. To assess the magnitude of factors, an operator typically conducts several tests. (1) Single-well or well-to-well tracer tests are used to assess oil saturation, transit times and reservoir heterogeneities. Remedial steps to narrow permeability contrasts with profile modification agents, such as the use of crosslinked polymers, are undertaken as necessary. (2) The design of a surfactant flooding formulation requires that field data and samples reflect the environment where the system is to be applied. The design of a flooding system is then optimized for the crude oil, brine, temperature, and rock where the system is to be applied. Field sampling to acquire representative samples is critical. Use of dead (loss of dissolved solution gas) stock tank oils, sodium chloride brines of equivalent salinity, and Berea sandstone cores rather than live crudes, field brines, and reservoir cores have led to systems that have failed in the field. (3) The chemical slug must be designed to withstand changes in salinity that occur in a reservoir. A review of previous analyses of injected and produced waters often indicates the range of salinity that the slug may encounter. Predictions can be made of the ion exchange anticipated when the surfactant slug contacts the rock and displaces divalent ions and increases the ionic strength of the brine. Effluents from corefloods are used to determine the transport times, slug separation, adsorption, and ion exchange. At lower surfactant concentrations the effect of dilution of the slug with connate water and migrating water can be evaluated for their effect on oil recovery and chemical consumption. (4) Native-state reservoir cores should be used as early as possible in the design of a chemical slug. The use of Berea sandstone or artificially oil-wetted Berea sandstone is for generic characterization, and all final designs of the chemical slug, selection of polymer, simulation, and economics need to be based on oil recoveries from native-state reservoir cores at anticipated reservoir conditions. Dilution, adsorption, partitioning, chromatographic separation of the chemical slug and emulsion characteristics of produced fluids are evaluated to assist in the design of a chemical slug and evaluation of the economics of the investment. Recently Lorenz has correlated field performance of many of the published surfactant-polymer chemical floods with the laboratory design procedures that were used and makes recommendations for improvement in the methodology which if implemented should reduce the technical and financial risk and improve the overall performance of chemical floods.<sup>11</sup>

Considering these limitations on chemical flooding systems, NIPER surveyed commercially available surfactants that could reduce oil-brine interfacial tension and might at the same time increase the

viscosity of a surfactant slug. This later restriction was imposed in an attempt to avoid the necessity of adding polymer to a surfactant slug, to avoid adverse surfactant-polymer interactions, and to reduce the number of components and/or cost of a chemical slug.

Amine oxides are one class of surfactants that meet some of the above requirements. At the onset of this research, one European patent claimed the use for chemical flooding but supported the claim with only one interfacial tension (IFT) measurement.<sup>12</sup> During this research, a second European patent was issued in which interfacial tension data were used to support the claim for use of amine oxides in chemical flooding.<sup>13</sup> In 1987, a topical report<sup>14</sup> on preliminary phase behavior and oil-displacement results was prepared, and the performance of these chemicals has prompted further study.<sup>15</sup>

Typical syntheses of amine oxides from a tertiary amine, dimethylalkyltertiary amine, or from bis(hydroxyethyl)alkyl tertiary amine are shown below.



The resulting amine oxides have a free electron pair on the nitrogen atom filling the gap in the electron octet of the oxygen atom. The polarity of the N-O dative bond in the amine oxide is shown schematically either as an arrow or as a partial charge separation,  $\text{N}^+ - \text{O}^-$ . The dipole moment of the bond has been calculated as 4.38 debye units.<sup>16</sup>

These surface-active compounds are nonionic at the pH of most reservoirs (pH 6 to 8) and become cationic in acid solutions below pH 3. The iron catalyzed decomposition of amine oxides is accelerated at low pH,<sup>16</sup> thus prohibiting the use of these surfactants in conjunction with carbon dioxide flooding. Amine oxides as a class of compounds have been widely used in detergent formulations along with anionic, nonionic, and cationic surfactants. Their principal use is film stabilization or viscosity building in cosmetic, household, and industrial products. The amine oxides with the alkyl chain length up to dodecyl,  $\text{C}_{12}$ , provide foam stabilization.<sup>17</sup> Amine oxides have recently been formulated into surfactant foam mobility-control and diverting systems for oil recovery.<sup>18</sup> Higher molecular weight amine oxides increase viscosity with or without the use of inorganic builders in aqueous solution and are used for this purpose in liquid laundry and hand soaps. They have been promoted as good wetting agents in

concentrated electrolyte solutions such as pickling baths for metal plating operations. Formulations containing amine oxides have been used for well workover fluids,<sup>19</sup> and ethoxylated amine oxides are used as corrosion inhibitors for nonferrous metals.<sup>13</sup> The largest volume application of amine oxides is in conditioners and antistatic agents such as fabric drying sheets for use in household laundry clothes dryers.

There are a number of reasons why amine oxides have potential as chemical flooding agents:<sup>14</sup>

1. There are two patents claiming use in EOR.
2. The substituent groups on the amine provide a wide variety of parameters that can be varied including alkyl chain length, degree of branching, and degree of ethoxylation or propoxylation in order to change the water solubility of the molecule.
3. Amine oxides show good reduction in surface tension in other applications.
4. These materials have been shown to increase viscosity in other applications and provide their own intrinsic viscosity. Amine oxides may be useful in mobility control and may avoid the use of polymers in injected slugs, thus eliminating adverse surfactant/polymer interaction.
5. Amine oxides have been shown to be compatible with other surfactants and show enhancement in performance in other applications.
6. A large potential volume is available although at present these surfactants are marketed as specialty rather than as commodity chemical. Applications in home laundry dryer sheets and fabric softeners consume most of the market.
7. The cost of amine oxides is not totally dependent on the cost of the volatile petroleum market because most amine oxides are based upon natural products, e.g., palm oil, tallow, soybean oil, etc.
8. There are a large number of amine oxide manufacturers, and the technology to produce amine oxides from amines is widely known. Some manufacturers may have economic or technical advantages in chemistry, plant size, and capacity to manufacture and ship concentrated solutions.

### **OBJECTIVE**

The objective of this research was to establish some of the constraints to using amine oxides as chemical flooding agents. Additional constraints include minimizing the number of components injected with emphasis on those systems that could provide viscosity to a chemical slug at a minimum surfactant concentration in an effort to develop cost-effective chemical flooding systems.

## ACKNOWLEDGMENTS

This work was sponsored by the U.S. Department of Energy under cooperative agreement DE-FC22-83FE60149 as task 5, project BE4A as outlined in the FY88 Annual Research Plan. The author wishes to thank NIPER employees Dr. Thomas E. Burchfield for his helpful advice, Charles Josephson and Sharon Munden for many of the phase behavior experiments, Dr. F. M. Llave for the computer programs used in analysis of the phase inversion temperature (PIT) scans, and Dr. Arden Strycker for computation of some of the phase behavior plots in the appendix. Brad Barber and Jay Mitchell who as U.S. DOE-supported Associated Western University Undergraduate Summer Fellows, worked on the PIT scans are thankfully acknowledged. We also thank Stepan, Witco, Akzo, Ethyl, Lonza, and Sherex chemical companies for providing samples of commercial surfactants used in the study, and especially Dr. Neil Jenny and the staff of the Sherex Laboratory, Janesville, Wisconsin, for the specialty amine oxides synthesized for this study.

## EXPERIMENTAL PROCEDURE

### Surfactant Composition

Since most amine oxides are derived from natural products, such as tallow, coconut, or palm oil, rather than from polymerization of ethylene or propylene, these surfactants contain a distribution of molecules in the hydrophobe as is shown in table 1.<sup>16</sup> The exception are those products from Ethyl Corporation which are based on ethylene polymerization and contain a narrow molecular weight distribution, i.e. Ethyl's bis(2-hydroxyethyl)tetradecylamine oxide has greater than a 98% tetradecyl alkyl chain length. Fractionation of natural product alcohols by distillation contributes significantly to increased cost; therefore, this study has concentrated on those surfactants that generate significant viscosity at a minimum cost per pound although no economics are presented in this report. This limitation imposed by the molecular properties of amine oxides in aqueous solution focused our research emphasis on those dimethylalkylamine oxides whose alkyl chain length is at least that of tetradecyl and other amine oxides of molecular structure that could balance the hydrophobic and hydrophylic properties similar to dimethyltetradecylamine oxide.

Most surfactants are mixtures in not only the carbon chain length of the hydrophobe but also have a distribution in the number of ethylene oxide units incorporated, and/or the degree of conversion of the nonionic to the anionic surfactant. This is also true for amine oxides in which conversion of the amine to the amine oxide leaves some (< 3%) unconverted amine in the commercial product. For household products, the residual amine content is usually limited to less than 2.5% because of skin and eye irritations caused by amines. Ethoxylation (EO) or propoxylation (PO) of amines both at nitrogen and within an alkyl chain give a distribution of isomers based upon the catalyst and operating conditions. The values listed in table 2 are average values.

TABLE 1. - Hydrophobe distribution (%) of amine oxides used in this study

Manufacturer/ Trade Name	Akzo Chemical Co. (Aromox )Series of Surfactants						Lonza Inc. (Barlox)	
Property / Designation	C/12-W	T/12	DMC	DMMC-W	DM16	DMHT	14	12
Mol wt (approx.)	304	366	244	239	285	307	249	240
HLB value	18.4		18.6	18.7	14.2	14.4		
SATURATED DISTRIBUTION								
Octyl, C8	6		6					
Decyl, C10	7		7	1				
Dodecyl, C12	51		51	70		3.5	40	69
Tetradecyl, C14	19	3	19	24	12	0.5	50	25
Pentadecyl, C15		0.5			1	31		
Hexadecyl, C16	9	29	9	5	75	1	10	6
Heptadecyl, C17		1			1	61		
Octadecyl, C18	2	20	2		11			
UNSATURATED DISTRIBUTION								
Tetradecenyl, C14		0.5						
Hexadecenyl, C16		2						
Octadecenyl, C18	5	22	5			2		
Octadecadienyl, C18	1	22	1			1		

Manufacturers add alcohols or other solvents to some amine oxides for ease of handling in both the oxidation step and transport. Many of the specialty amines supplied by manufacturers were water based for the purpose of this study so that the effect of adding various alcohols could be studied. Although the amine oxide samples did not contain appreciable amounts of salt, they did contain free amine (less than 2.5%) and hydrogen peroxide (less than 0.34%). An abridged summary of the amine oxides acquired and surveyed during this study and grouped by manufacturer is given in table 2. The active concentrations of the amine oxide and cosolvent (alcohol) were determined from product literature, material safety data sheets (MSDS), and correspondence with manufacturers. For those that do not list a cosolvent, water was the dispersant and constitutes the balance of the material.

Amine oxide solutions and other surfactants were prepared as concentrates for PIT, viscosity, phase behavior, and screening tests and are on a weight per unit volume (g/100 mL) basis, unless otherwise noted. Salinities are those of the aqueous phase. Alkanes and surfactants including the amine oxides were not purified, and analyses of the amine oxides, as reported by the manufacturers, are shown in table 2. Many of the ethoxylated materials are experimental and meet requirements of the TSCA Section 5(h) R&D Exemption. The amine oxide concentrates (>20%) are both severe skin irritants and

TABLE 2. - Names, structures, and composition of amine oxides surveyed

Manufacturer Tradename	Chemical Structure			EO Groups (R2 + R3)	AO Active %	Cosolvent		Ref.	CAS No.
	R 1	R 2	R 3			CoS	%		
AKZO CHEMICAL									
AROMOX SERIES OF SURFACTANTS									
DM16-W	Tallow	CH 3	CH 3		30			MSDS	
DM16	Tallow	CH 3	CH 3		40	IPA	36	MSDS	7128-91-8
DMHT	H Tallow	CH 3	CH 3		40	IPA	36	MSDS	
DMHT-W	H Tallow	CH 3	CH 3		10	I		MSDS	
DMMC-W	Coco	CH 3	CH 3		30			MSDS	61788-90-7
T/12	Tallow	CH2CH2OH	CH2CH2OH	2	50	IPA	25	MSDS	61791-44-4
C/12-W	Coco	CH2CH2OH	CH2CH2OH	2	40				61791-47-7
T/12-W	Tallow	CH2CH2OH	CH2CH2OH	2					
DMC	Coco	CH3	CH3		40	IPA	36	MSDS	61788-90-7
SHEREX CHEMICAL									
VAROX SERIES OF SURFACTANTS									
185-E	C8-C13 (PO)	CH2CH2OH	CH2CH2OH	2	50				
188-E	Coco (PO)	CH3	CH3		35+-5			MSDS	
DP SC 192-103		C8-C10(PO)	CH2CH2OH		CH2CH2OH		40+-5		
U 202	HTallow	CH2CH2OH	CH2CH2OH	2	19.9				
T 202	Tallow	CH2CH2OH	CH2CH2OH	2	31.4			MSDS	
EPSC 192-134	Coco	Coco	CH3		85+-10			Tech Data Sheet	
DPSC192-193	C12-15 (PO)	CH2CH2OH	CH2CH2OH	2	80			MSDS	68910-38-3
EPSC 233-28	C8-C10	C8-C10	C8-C10		90			Tech Data Sheet	
ETHYL CORPORATION									
	C14	CH2CH2OH	CH2CH2OH		33.9			MSDS	
	C10	C10	CH3		77.9			MSDS	
LONZA									
BARLOX 18S	Steryl	CH3	CH3		25			MSDS	2571-88-2
BARLOX 16S	Cetyl	CH3	CH3		30			MSDS	7128-91-8
BARLOX14	Myristyl	CH3	CH3		30			MSDS	3332-27-2
BARLOX 12	Coco	CH3	CH3		30			MSDS	61788-90-7
STEPAN									
Ammonyx CO	Cetyl	CH3	CH3		30			MSDS	7128-91-8
Ammonyx MO	Myristyl	CH3	CH3		30			MSDS	3332-27-2

moderate to severe eye irritants; but at anticipated levels of application, i.e concentrations of 3% or less (in water), they are nonirritating or only mildly irritating to skin or eyes.

### **Viscosity Scans of Amine Oxides**

The viscosities of the amine oxides or the amine oxides in combination with other solvents or surfactants were measured using a Brookfield LVT cone and plate viscometer and converted to a shear rate of  $6 \text{ sec}^{-1}$  for comparison.

### **Phase Inversion Temperature Measurements**

Phase inversion temperature (PIT) measurements were made using the NIPER automated system for PIT measurements.<sup>20</sup> The PIT of a hydrocarbon/brine/surfactant system indicates the potential of a minimum in interfacial tension at that temperature and shows the transition from water external to oil external emulsion or visa versa. Lowering of interfacial tension improves mobilization of oil trapped in the pores in rock matrix of oil reservoirs by increasing the capillary number. Since reservoirs are isothermal, the PIT is a useful parameter for selecting surfactants for a given reservoir, as has been discussed in a series of papers by Salager.<sup>21-25</sup>

For nonionic surfactants at temperatures below the PIT, the surfactant partitions preferentially into the aqueous phase, and emulsions formed between the two phases are predominantly oil-in-water emulsions. At the PIT, the electrical conductivity of the mixture decreases markedly, sometimes within a few tenths of a degree. Above the PIT, the mixture is an oil-external, predominantly water-in-oil emulsion, with low electrical conductivity.

### **Phase Behavior**

Phase partitioning tests, salinity scans, temperature scans, and equivalent alkane carbon number (EACN) scans of amine oxide formulations with and without added alcohol were conducted using sealed 10-mL disposable glass pipets. Equal volumes of brine containing the surfactant formulation and oil were placed in a pipet. The tubes were sealed and then heated to temperature in a constant temperature bath. The tubes were vigorously shaken and allowed to stand overnight. Phase volumes were read and the tubes returned to the bath and reread the following week or until constant readings were obtained (this required from hours to months depending upon the viscosity of the solutions, the density difference between phases, the interfacial viscosity, and the proximity to the optimal salinity).

The method used in this study for determination of phase behavior has been described in more detail in a series of U.S. patents by Glinsmann,<sup>26-27</sup> and Hedges,<sup>28-30</sup> but it is also the basis for much of the work reported in the literature before these patents were issued, including reviews by Shah and

Schechter<sup>31</sup> and Shah.<sup>32</sup> Solubilization parameters calculated for the three-phase systems are summarized in the appendix.

### **Interfacial Tension**

Interfacial tensions (IFT), were measured with a University of Texas thermostated spinning drop tensiometer. The results of phase behavior tests and the calculations of solubilization parameters were often checked by the spinning drop method. The IFT's of all surfactant formulations were determined before injection into cores.

### **Surfactant Adsorption**

The adsorption of amine oxides was determined on three different minerals: quartz, kaolinite, and montmorillonite at 24° C by titrating a suspension of each mineral in brine with the surfactant solution. Surfactant concentration was measured by surface tension measurements with a Du Nouy ring tensiometer.

### **Surfactant Stability**

The stability of selected amine oxides was conducted using static bottle tests. Surfactant stability was assessed by noting the color and the change in viscosity of the formulations with time.

### **Coreflood Experiments**

The following procedure was used in preparing the water-wet Berea sandstone cores used for surfactant flooding. Berea cores 10 inches long and 1.5 inches in diameter were weighed to determine dry weights before saturation with brine of the desired salinity. The cores were placed in an evacuation chamber, and a vacuum of about 1 mm was pulled on the cores for at least 2 hours. The cores were saturated under partial vacuum with degassed brine and allowed to remain under vacuum for more than 1 hour. The cores were removed from the evacuation chamber and weighed to determine saturated core weight. The pore volume of the cores was calculated by the relationship: brine-saturated core weight (g) - dry core weight (g) divided by the density of the brine (g/mL) equals the core pore volume (mL). The cores were then mounted in a thermostated Hassler sleeve while still saturated with brine, and brine (>20 pore volumes) was pumped through the cores before determining the original permeability to brine which usually required at least 12 hours.

The brine-saturated cores were flooded with oil at >30 ft/d to remove all displaceable water. The oil floods were carried out using a recycling oil system and required >24 hours. The total water displaced during oil floods was used to calculate oil saturations,  $S_{oi}$ , (original oil saturation). Optionally, oil permeabilities were determined in a manner analogous to that used above for establishing the original permeability to water.

The oil-saturated cores were waterflooded at 3 to 5 ft/d, until the effluent water-oil ratio was greater than 200:1. The total oil displaced was measured, and  $S_{OW}$  (oil saturation at the end of the waterflood) was calculated. The volume of residual oil remaining in the core was calculated by subtracting the oil volume displaced by the waterflood from the water volume displaced by the oil flood. If desired, the water permeability after waterflood was determined in a manner analogous to that used above for original permeability to water. Cores were routinely conditioned in this manner before surfactant flooding tests were performed. At this point, the cores simulated an oil reservoir at residual oil saturation.

The surfactant slug containing the amine oxide was injected at a slower rate, corresponding to typical field flow rates of 1 ft/d for the pore volume specified. The slug optionally contained a mobility buffer (polymer) or was followed by a mobility buffer. Oil recovery from the core was measured to determine  $S_{OC}$ , final oil saturation after chemical flooding. Oil recovery efficiency of the chemical flood,  $R_e$ , was calculated as  $(S_{OW} - S_{OC})/S_{OW} \times 100$ .

Berea sandstone cores were used for all experiments. Oil-wet Berea cores were prepared using a vacuum saturation technique in which the core was heated under vacuum to 150° C overnight, cooled and then a 7% solution of chlorotrimethylsilane in hexane was introduced into the system while under vacuum. The cores remained in contact with the solution for at least 48 hours, then the vacuum was released, and the cores were dried in a hood.<sup>34</sup> Cores were flushed with multipore volumes (>100 PV) of water, dried in an oven overnight (50° C), and prepared as described above for a water-wet Berea core.

## **EXPERIMENTAL RESULTS AND DISCUSSION**

### **Choice of Test Conditions**

The test conditions that were chosen for most of the experiments in this study evolved from previous work on surfactants that may have potential application in the Wilmington (CA) field, and the North Burbank (OK) field. The temperature of 40° C also represents a number of midcontinent reservoirs that were selected as being amenable to chemical flooding.<sup>10-11</sup> Many of the patents on chemical flooding systems issued to Phillips Petroleum Company used North Burbank brine or mixtures of that water and freshwater at a temperature of 40° C, and used decane as a representative oil during testing. Thus, a large body of data on the performance of other surfactant systems at these conditions was available so that surfactants could be compared.

### **Coreflood Experiments**

Figure 1 shows the recovery efficiency from a series of corefloods with increasing slug size conducted in 10-in. water-wet Berea sandstone cores using 3% DMHT-W and 3% IBA as a formulation to

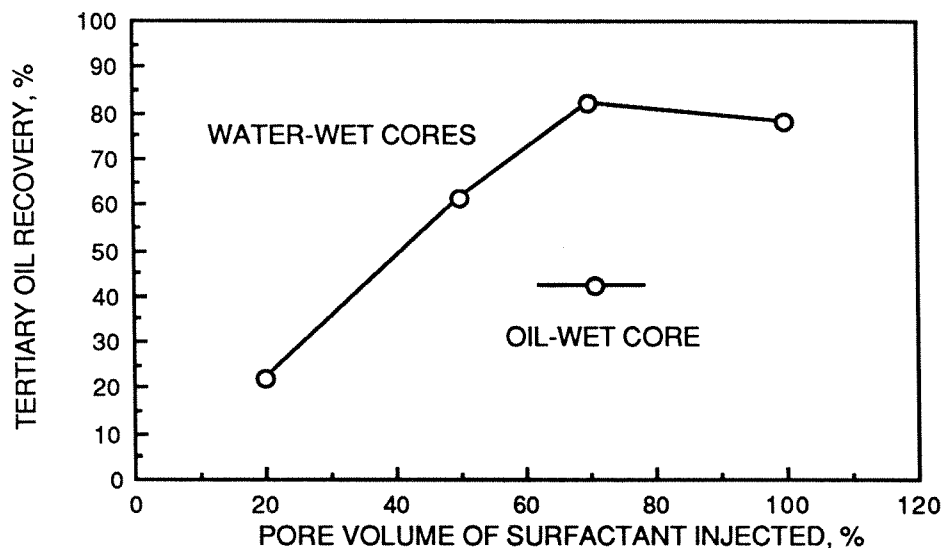


FIGURE 1. - Oil recovery efficiency from 3% DMHT-W and 3% IBA displacing decane.

displace decane. The figure expands on previously reported work.<sup>14</sup> Corefloods were conducted at 50° C at 1 ft/d at a constant salinity of 8.1 % NaCl as the brine. The formulation was prepared by stirring overnight and filtering through 2.5-micron filter paper. The IFT of the formulation vs. decane was 18 millidyne/cm at 50° C and the dispersion had a viscosity of 2.4 cP. A mobility buffer ( 1.2 pore volumes) of Flocon 4800 R biopolymer, manufactured by Pfizer, having a viscosity of 12 cP, was injected to displace the surfactant slug. This 20% pore volume slug of surfactant recovered 22% of the decane remaining in place after waterflood. Despite the high solubilization parameter vs. decane (30), low IFT (18 millidyne/cm), and the wide salinity tolerance that the formulation possesses and the mobility control slug behind the surfactant, the surfactant stripped oil rather than banking oil in corefloods. An artificially oil-wet Berea sandstone core<sup>34</sup> gave only 52% recovery (figure 2) as compared with 81% recovery from a water-wet core for the same pore volume of surfactant injected and exhibited similar oil stripping behavior. The comparison of water-wet and oil-wet results are not direct comparisons because the oil-wet coreflood was conducted at 9.2% NaCl at 40°C (IFT of 4.2 millidynes/cm) and omitted polymer from the polymer drive fluid. The multiple pore volumes of fluid required for oil recovery from the oil-wet Berea core is typical of the oil stripping observed when the amine oxide was used without a more viscous polymer based mobility control agent behind the surfactant slug. This is not a direct comparison because the coreflood experiment in the oil-wet core was conducted at 9.2 % NaCl at 40° C with an IFT of 4.2 millidynes/cm and omitted polymer in the drive fluid.

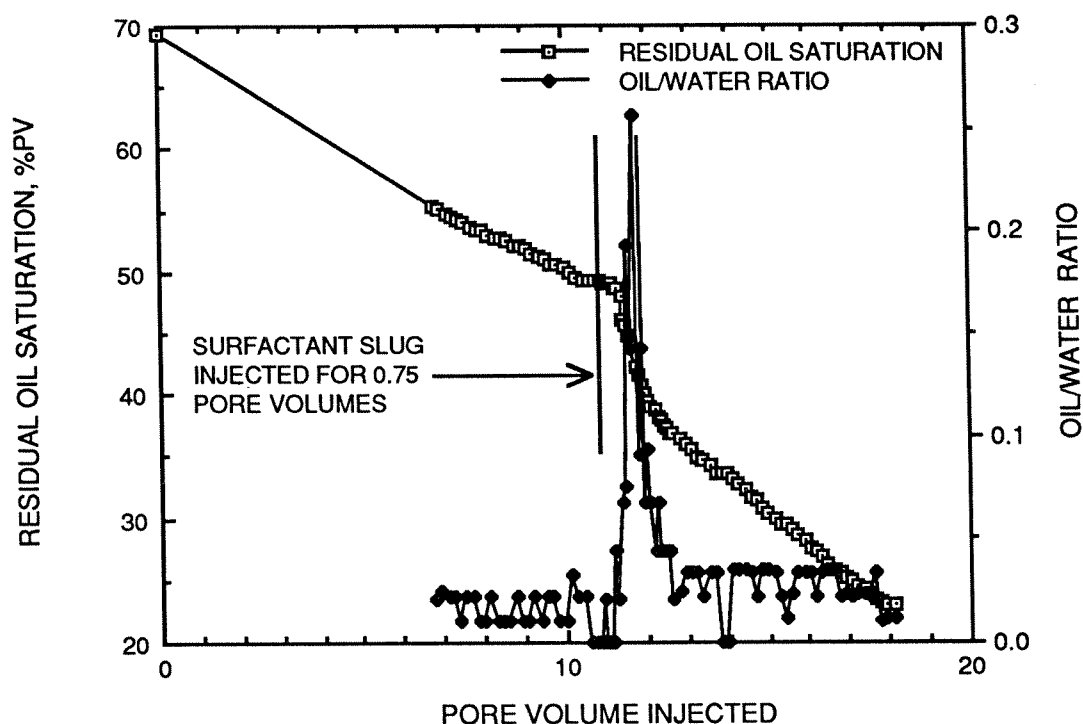


FIGURE 2 - Oil recovery efficiency of 3% DMHT-W and 3% IBA displacing decane from an oil-wet core.

### Surfactant Adsorption

The adsorption of DM16-W by three different minerals: quartz, kaolinite, and montmorillonite was determined at 24° C by titrating a suspension of each mineral in NBU brine with the surfactant solution. Surfactant concentration was measured by surface tension measurements with a Du Nouy ring tensiometer, which was calibrated by titrating a sample of NBU brine without added mineral. Surface tensions were repeatable to within  $\pm 0.5$  dyne/cm over the range of 30 to 60 dynes/cm. The solution was composed of 3 wt % DM16-W, 3 wt % IBA, and 94 wt % NBU brine and were conducted at a liquid to solid ratio of 20. Plateau adsorption increased in the following order: quartz, kaolinite, and montmorillonite which also reflects the increase in surface area<sup>34</sup> for these minerals. These adsorption values are in agreement with adsorption of other surfactants used in chemical flooding,<sup>34</sup> as shown in table 3.

### Viscosity Scans of Amine Oxides

The viscosities of 1% solutions of a series of dimethylalkylamine oxides in seawater were measured at various temperatures with a Brookfield viscometer. The results showed that high viscosities are produced with dimethylalkylamine oxides having an alkyl chain length greater than that of tetradecane, as shown in figure 3.

TABLE 3. - Adsorption of DM16-W

Mineral	Adsorption, grams surfactant/gram of mineral
Quartz	0.0021
Kaolinite	0.013
Montmorillonite	0.082

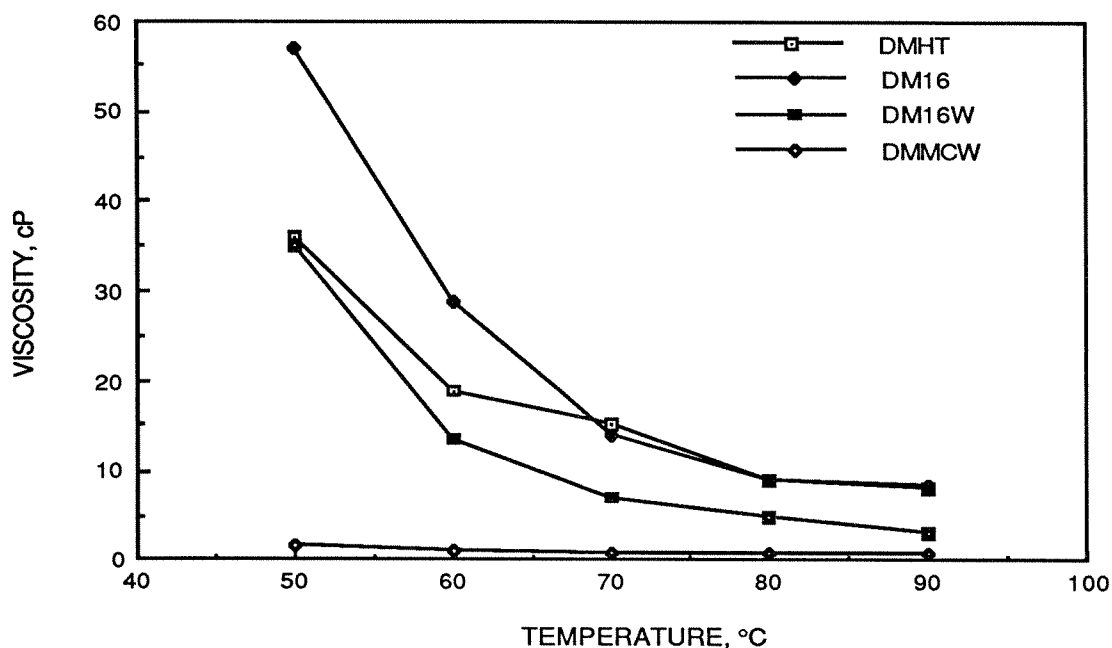


FIGURE 3. - Viscosity of 1% amine oxides solutions in seawater.

### Stability Tests of Amine Oxides

The stability of amine oxides was studied in synthetic seawater at ambient temperature. A series of amine oxides and isoamyl alcohol, IAA, (3 % : 3 %) were evaluated by measuring the viscosities of the solutions over a 4-month period. The exceptions were T202 and U202 which did not contain alcohol. These solutions were sealed in glass ampules, but no provision was made to exclude air. The ampules were then opened at 7, 14, 28, and 120 days, and the viscosities of the solutions were measured and converted to a shear rate of  $6 \text{ sec}^{-1}$ . The results are shown in figure 4. The viscosities of the solutions increased as the alkyl chain length in the dimethyl alkyl amine oxides increased. Those with an alkyl chain length of at least tetradecyl, C<sub>14</sub>, increased viscosity. With the exception of DMHT-W, all the viscosities of solutions decreased with time and the viscosities of solutions with low viscosities decreased or remained nearly the same as that of seawater.

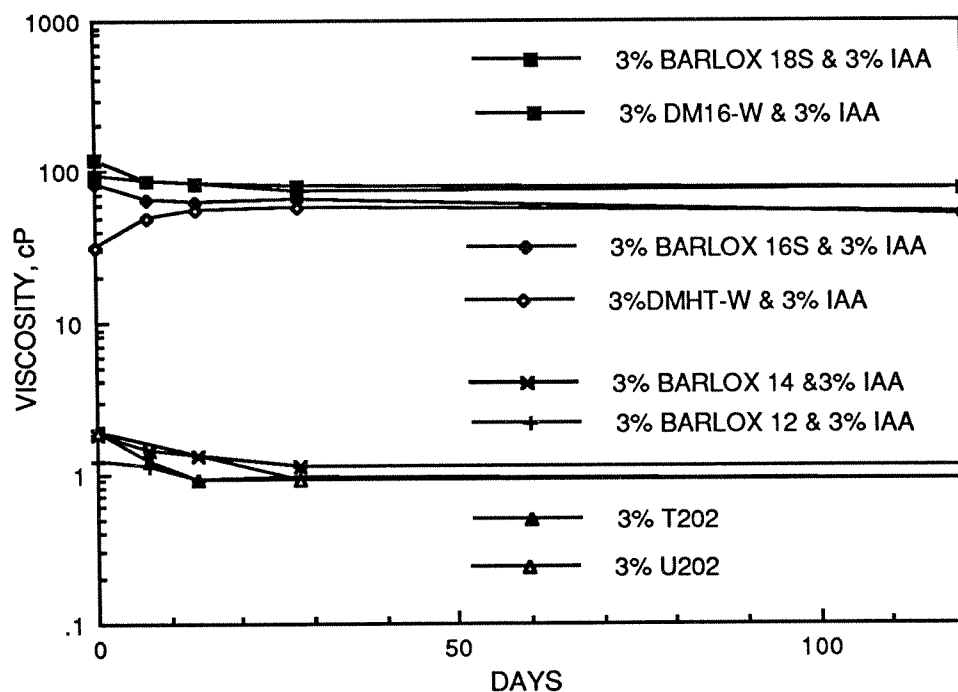


FIGURE 4. - Loss of viscosity with time for amine oxides.

The long-term stability of some amine oxides and ethoxylated amine oxides in seawater at 40° C were evaluated over a 6-month period, and an example of their performance is listed in table 4. Three sets of vials were prepared: 5 mL of 3% surfactant and 1 g of crushed Berea sandstone in screw cap bottles (no provisions to exclude oxygen); 10 mL of 3% surfactant in glass ampules and 1 g of crushed Berea sandstone (sealed under vacuum); and 10 mL of 3% surfactant in glass sealed ampules under nitrogen. Stability, as measured by the viscosity and appearance of the surfactant, was determined for the vials at 1 day, 1 week, 1 month, 3 months, and 6 months (table 3). Screw cap bottles containing crushed Berea sandstone formed a brown precipitate on standing at 40° C, and their viscosities dropped to that of the brine within 3 months. The ethoxylated amine oxides changed color more rapidly, and on opening, the heated screw cap bottles containing Berea sandstone and the amine oxides exhibited a strong odor of amine. The heated ampules sealed under partial vacuum containing Berea sandstone and amine oxide survived significantly longer with light coloration in the ampule and a slight amine odor at 3 months. The ethoxylated amine oxide, T202 as well as the entire series of ethoxylated and propoxylated amine oxides synthesized for this study, exhibited a dark brown colored precipitate and produced a strong amine odor after only a few weeks under simulated reservoir conditions. Formulations containing alcohols and amine oxides such as the data shown for Barlox 16S in table 4 survived appreciably longer, and only a slight odor

TABLE 4. - Viscosity of amine oxides at 40° C (viscosity in cP)

Time, days	Barlox 16S			T202		
	Berea sandstone		Ampule - N2	Berea sandstone		Ampule-N2
	Bottle	Ampule		Bottle	Ampule	
1	83	85	90	1.9	1.9	1.9
30	1.1	6.2	87	1	1.1	1.2
90	1.1	1.8	77	2	1	1.1
180	1	1.6	71	Sludge	Sludge	1

and color change were evident at 6 months. The base case samples sealed under nitrogen and containing only the amine oxides showed some viscosity loss with time and maintained a higher viscosity than ampules containing Berea sandstone. A reservoir application would be expected to exceed 6 months and contain some dissolved oxygen. The above experiments did not duplicate actual reservoir conditions, but the results indicate that the ethoxylated and propoxylated amine oxides tested would probably not survive and that formulations containing alcohol should have better potential for maintaining a viscous surfactant slug. Further studies are needed to conclusively demonstrate that they can survive the pH and oxidation-reduction reactions of a specific reservoir including surface tanks, flowlines and injection tubing, and the nearwell oxidizing environment caused by low concentrations of oxygen being transported as dissolved gas in the injected brine before the surfactant contacts the bulk of the reservoir.

#### Phase Inversion Temperature Measurement

The effects of pH, salinity, and alkane carbon chain length on the phase inversion temperature, PIT, of the surfactant system composed of 3% T202 and 3% IBA were previously reported.<sup>14</sup> The formulation vs. decane, at constant salinity, showed a sequential drop in PIT with pH as well as a narrowing of the PIT transition range. Thus, the PIT's reported herein are at the pH of the aqueous solution as mixed, and no attempt has been made to adjust the pH. The pH values of most amine oxides as a 1% solution are between 6.5 and 7.5. Selection of amine oxides for a specific reservoir application will need to accommodate not only the specific pH but also the eH of the reservoir in the screening tests to select the appropriate formulation. As with all amine oxides, they become increasingly cationic as the pH decreases.

The effect of alkyl chain length on the PIT of 3% DM16-W and 3% IBA is shown in figure 5. The series parallels the results obtained with T202 showing that higher PIT's are obtained with longer alkanes and that for the same alkane the PIT decreases with increasing salinity.

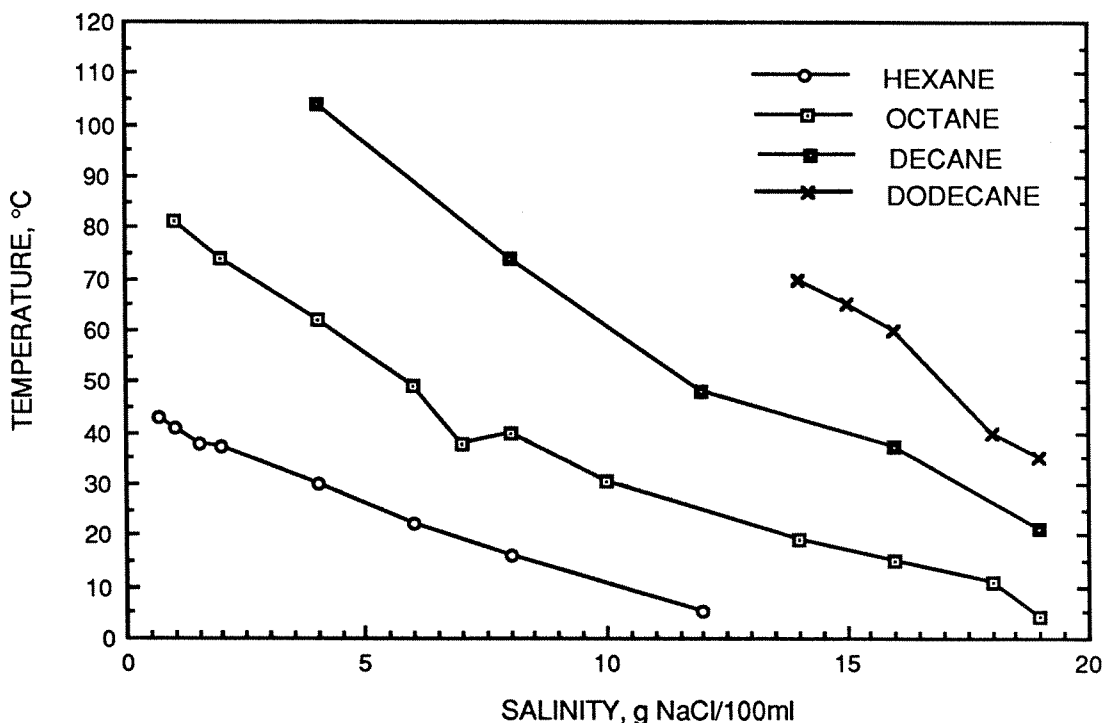


FIGURE 5. - PIT of 3% DM16-W and 3% IBA showing the effect of alkyl chain length and salinity.

### Phase Behavior

Phase behavior scans of amine oxides with both alkanes and a limited number of crude oils showed that formulations containing dimethylalkylamine oxides with alkyl chain lengths up to C<sub>18</sub> showed two phase behavior at salinities through saturated NaCl with the surfactant remaining in the aqueous phase or forming a third phase. The results of these phase behavior studies are summarized in table 5. The table is formatted similar to the NIPER surfactant data base and lists the surfactant manufacturer, surfactant trade name, surfactant composition, percent actives and cosolvent as delivered, surfactant formulation and percent, alcohol and percent, hydrocarbon used for phase behavior, temperature of phase behavior study, phase behavior data including width of the 3-phase window from lowest salinity to highest salinity, salinity at which a equal solubilization occurred, the solubilization parameter at maximum ( $\delta$ ), and reference to the figures in the appendix of this report where the phase behavior plots can be found. When the surfactant in the phase partition tests, as listed in table 5, are described as "Too water soluble at a specific temperature," the notation means that with the alkane listed and at less than a specific salinity the surfactant remains in the aqueous phase, a II<sup>-</sup> phase.

### Amine Oxides with Alcohols

The effects of molecular weight and chain length of the cosolvent alcohol on phase behavior of amine oxides are shown in table 5. As the chain length of the alcohol increases, the salinity tolerance of

TABLE 5. - Phase behavior of amine oxides surveyed

Surfactant Formulation				Alkane	Temp. °C	Three phase window			Optimal salinity % NaCl	Solubilization parameter	Figure ref.
Amine Oxide	Conc., %	Alcohol	Conc., %			Low % NaCl	High % NaCl	Range % NaCl			
AKZO (AROMOX)											
DM16-W	3	IPA	3	Decane	40	2.1	3.9	1.8	3.1	27	
	3	IBA	3	Decane	40	9.3	12.9	3.6	10.8	10.8	
					45	7.6	12.8	5.2	9.9	15	
					50	6.5	12.4	5.9	9.25	12.5	
					55	6.2	11.8	5.6	7.8	13	
					60	5.9	10.2	4.3	7.5	21	
	3	IAA	3	Decane	6	3	>5	>2	>4		
					13	0	3.6	3.6	1.25	17	
					24	0	1.6	0.4	0.4	22	
	3	IPA	3	Octane	40	4.5	12	7.5	9.2	16	
3	IAA	3	Octane	40	1.7	3.8	2.1	2.6	25		
DM16	3			Decane	40	2.1	3.8	1.7	3.1	21	
DMHT-W	3	IAA	3	Decane	40	0	1	1	0.45	22	
	3	IBA	3	Decane	40	5.6	18	12.6	9.2	30	
DMHT	3	IBA	3	Decane	50	5.4	17	10.6	8.1	31	
	3	IBA	3	Dodecane	40	1	2.5	1.5	2.1	12	
	3	IBA	3	Decane	40	2.2	4.1	1.9	2.8	16	
	3	IPA	3	Octane	40	5	14	9	6.9	18	
DMC-W	3	IAA	3	Decane	40	11.4	20	9.6	16	19	
DMC 3				Decane	40	21	>30	>9	>28		
DMMC-W	3	IAA	3	Decane	40	9.5	23	13.5	17.5	9	A-6
SHEREX (VAROX)											
185-E	3	Too water soluble at 80° C in C10-C16<30% NaCl, with C8~30 NaCl gives 3 phase									
188-E	3	Too water soluble at 50° C in C8, C10, C12,C16 <29% NaCl									
U202	3	IBA	3	Dodecane	50	1	14	4.8	13	11	A-1
	3	IBA	3	Decane	50	>20					
	3	IBA	3	Octane	50	>30					
	3	IPA	3	Dodecane	50	>20	30	>9			
	3	IPA	3	Decane	50	18	>20				
	3	IPA	3	Octane	50	9	>20	>11	16	8	
T202	1	IBA	3	Decane	40	0.35	0.7	0.3	0.3	17	A-2
DPSC192-193	3	Too water soluble at 80° C in C8, C10, C12, C16 <30% NaCl									
ETHYL (AMINE OXIDES)											
C14		No phase behavior studies conducted.									
C10		Surfac tant is too oil soluble in brines to prepare dispersions.									
LONZA (BARLOX)											
18S	3	IAA	3	Decane	40	0	1	1	0.5	20	
	3	IBA	3	Decane	40	11	17	6	15	17	
16S	3	IAA	3	Decane	40	3.5	12	8.5	7	26	
	3	IBA	3	Decane	40	8	18	10	15	19	
14	3	IAA	3	Decane	40	6.5	18	12.5	15	20	
STEPAN (AMMONIX)											
CO	3	IAA	3	Decane	40	0.1	3.5	3.4	2.6	22	
MO	3	IAA	3	Decane	40	4.5	17	11.5	15	21	

the three-phase system decreases. Increasing the temperature of the system shifts the three-phase region to lower salinity. The optimal salinity decreases as the EACN decreases. For most of the formulations, the solubilization parameter is high indicating a low IFT and therefore oil recoveries should be higher than those obtained. Several of the manufacturers products with approximately the same composition exhibited similar phase behavior.

### **Ethoxylated Amine Oxides**

Based on our previous work on amine oxides,<sup>14</sup> the potential for incorporating the alcohol functionality into the amine oxide by either ethoxylation, propoxylation or both was one way to make a cosurfactant free chemical flooding surfactant that incorporated a balanced hydrophobic and hydrophylic functionality. The phase behavior of a few amine oxides that incorporated the alcohol functionality into the structure (ethoxylation or propoxylation) was determined. Most of the amine oxides supplied by manufacturers yielded low viscosity solutions, but had high salinity tolerance. Because of the poor stability shown in simulated reservoir conditions and low viscosity, research was refocused on the amine oxide blends with short chained alcohols.

### **Petroleum Sulfonates and Amine Oxides**

A series of phase partitioning experiments shown in table 6 were conducted to evaluate the effect of amine oxides on the phase volume behavior with a known surfactant system, Witco TRS10-410, a petroleum sulfonate. When IBA is replaced in part (0.1, 0.5, and 1.0%) with the amine oxide T202, the three-phase region shifts to lower salinity (figs. A-7 and A-9, A-7 and A-10, A-7 and A-11), resulting in a narrower width to the three-phase region and quadruples the solubilization parameter. When TRS10-410 is replaced in part with T202, the three-phase region again shifts to lower salinity (figs. A-3 and A-7) but decreases the width of the three-phase region and the same solubilization parameter.

When TRS10-410 is replaced by the amine oxide DM16-W at a low substitution level (0.1%), the three-phase region shrinks and shifts to lower salinity, and the solubilization parameter increases (A8 and ref. 30). At the higher replacement level of 1% DM16-W, the lower limit of the three-phase window was above 2% NaCl, and the aqueous phase became very viscous at 50° C. Thus, both higher temperatures and longer equilibration times would be required to define limits of the three-phase region.

In the series where equal concentrations of TRS10-410 and IBA (3% : 3%) were equilibrated with decane, the phase-partitioning temperature scan showed the highest solubilization parameter (14) and was achieved with the system that had the narrowest three-phase window at 40° C. If the concentration of both TRS10-410 and IBA were reduced to 1.5%, then the width of the three-phase region decreases.

TABLE 6. - Phase behavior of mixed amine oxide - TRS10-410 surfactant systems

TRS	Surfactant formulation				Oil or alkane	Temp., °C	Three-phase window			Max sol % NaCl	$\delta$	Fig. ref.	
	Conc. Amine % Oxide	Conc., % Alcohol	Conc., %	% NaCl			Range % NaCl						
				Low				High					
3			IBA	3	Decane	22	0.95	1.90	0.95	1.4	10	----	
3			IBA	3	Decane	40	0.78	1.18	0.4	0.92	14	(30)	
3			IBA	3	Decane	50	1.10	1.90	0.8	1.55	6	A-7	
1.5			IBA	1.5	Decane	50	0.80	1.10	0.3	0.95	12	A-4	
3	T202	0.1	IBA	2.9	Decane	50	0.60	1.00	0.4	0.8	13	A-9	
3	T202	0.5	IBA	2.5	Decane	50	0.60	0.80	0.2	0.68	15	A-10	
3	T202	1	IBA	2	Decane	50	0.35	0.80	0.45	0.6	22	A-11	
				3	Decane	50	0.70	1.40	0.7	0.8	7	A-3	
2.5	T202	0.5	IBA	3	Decane	50	0.20	0.81	0.61	0.5	4.5	A-12	
2.5	T202	0.5	IBA	3	Decane	80	0.40	0.75	0.35	0.5	9	A-13	
2.5	DM16-W	0.1	IBA	3	Decane	50	0.50	0.80	0.3	0.65	17	A-8	
2	DM16-W	1	IBA	3	Decane	50	>2	Very viscous, higher temp. needed.					A-5

The position of the maximum of the solubilization parameter, and magnitude of the solubilization parameter were nearly identical with the higher concentration system (figs. A-4 and ref. 30). However, the equilibration time to reach equilibrium was greatly reduced and was achievable at 50° C within 3 days, whereas the higher concentration systems required 3 weeks.

### SUMMARY

Based upon the results of the FY87 research on amine oxides, a continuation of that effort was proposed as task 5 in project BE4A of the FY88 Annual Research Plan.<sup>36</sup> It was hoped that the series of ethoxylated and propoxylated amine oxides synthesized for this work by Sherex would allow incorporation of water solubility that the alcohol provided in the blends of amine oxide and alcohol. Both phase behavior and PIT scans were conducted but not reported because these surfactants were not suitable for long-term applications in reservoirs, and research on these materials was discontinued.

The results of this study of amine oxides as chemical flooding agents are listed in order of priority.

1. Research on the use of amine oxides and ethoxylated or propoxylated amine oxides as primary surfactants for chemical flooding EOR should be suspended.
2. Dimethylalkylamine oxides are useful as cosurfactants and viscosifiers in formulations with other surfactants for chemical flooding EOR but the use of ethoxylated and propoxylated amine oxides should be avoided due to the decomposition of these more water soluble amine oxides under reservoir conditions.

3. Oil recovery from phase behavior optimized amine oxide-alcohol systems is dependent upon the quantity of surfactant (concentration times pore volumes injected) in floods designed at constant salinity and require excessive amounts of surfactant to be economically competitive with other surfactants that can function at the same salinity.
4. Dimethylalkylamine oxides with an alkyl group longer than that of tetradecane can be used to provide mobility control to a chemical slug or for mobility control in place of polymers, however they require concentrations that are usually greater than 1% whereas comparable viscosities can be formulated from polymers at concentrations around 1000 ppm.
5. Three-phase behavior is achievable with amine oxides over a broad range of salinity, either with systems that incorporate an alcohol functionality into the molecule by ethoxylation or by addition of short-chain alcohols.
6. The solubilization parameters for amine oxide-alcohol blends are relatively high (low interfacial tensions).
7. Amine oxides recover more oil from water-wet cores than from oil-wet cores.
8. All of the amine oxide solutions showed loss of viscosity with time, and the ethoxylated amine oxides showed a more rapid loss of viscosity and decomposition of the surfactant, especially in the presence of oxygen and Berea sandstone. Both pH and oxidation/reduction potential of an application must be established before using amine oxides.

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# APPENDIX

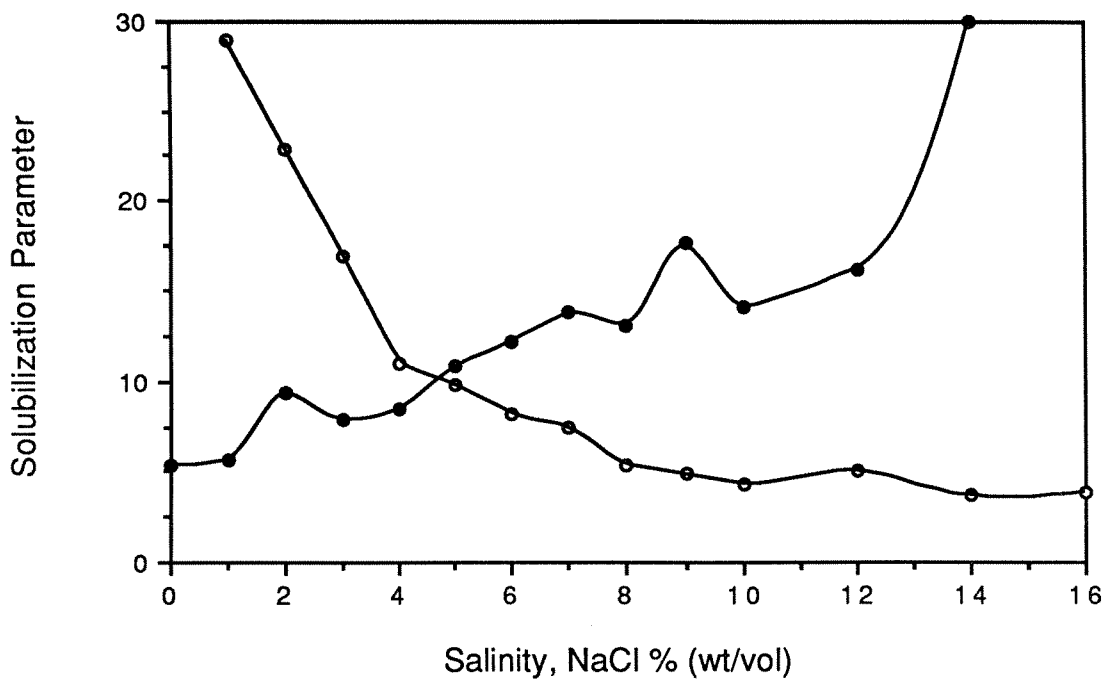
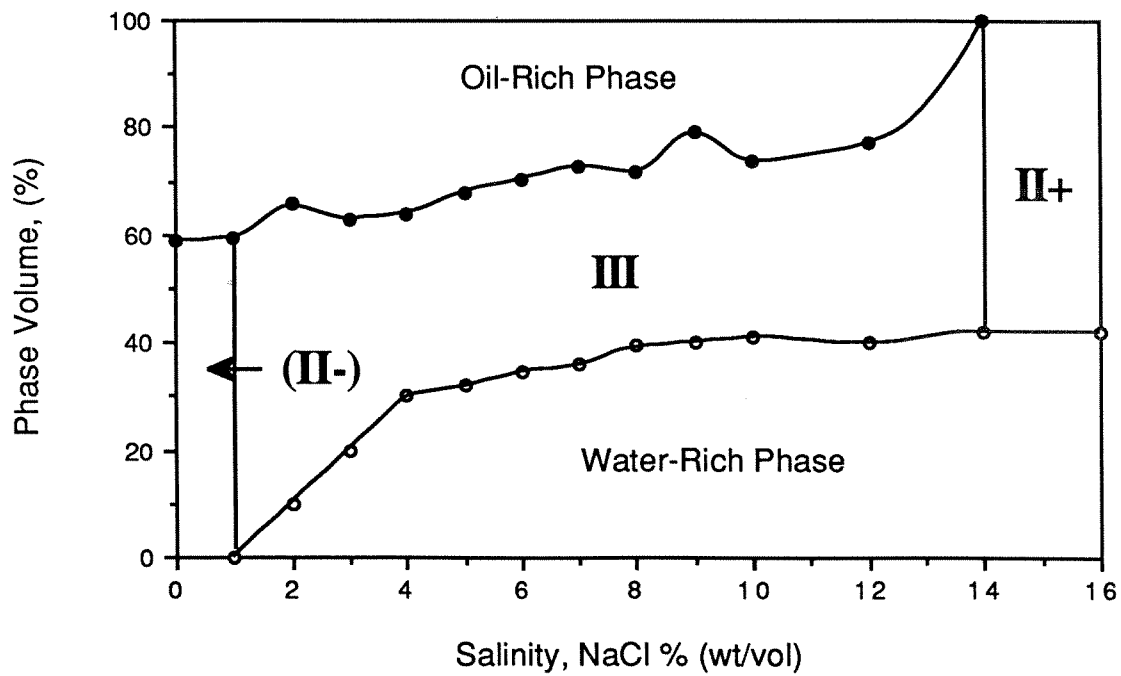


FIGURE A-1. - Phase behavior of 3% U202 and 3% IBA with dodecane at 50°C.

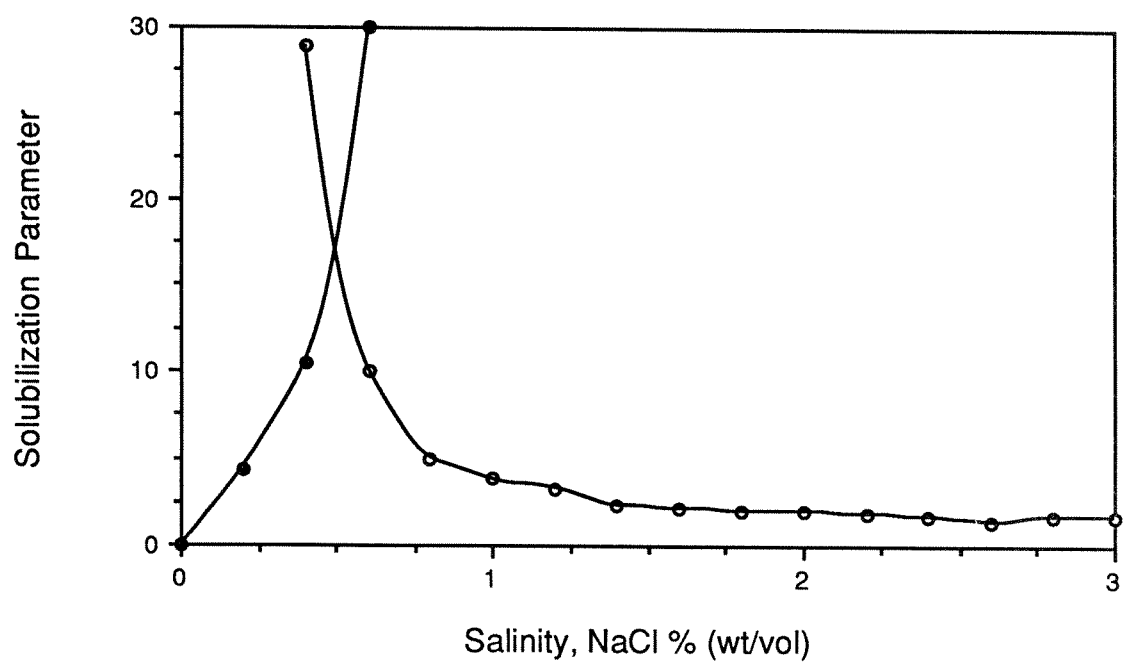
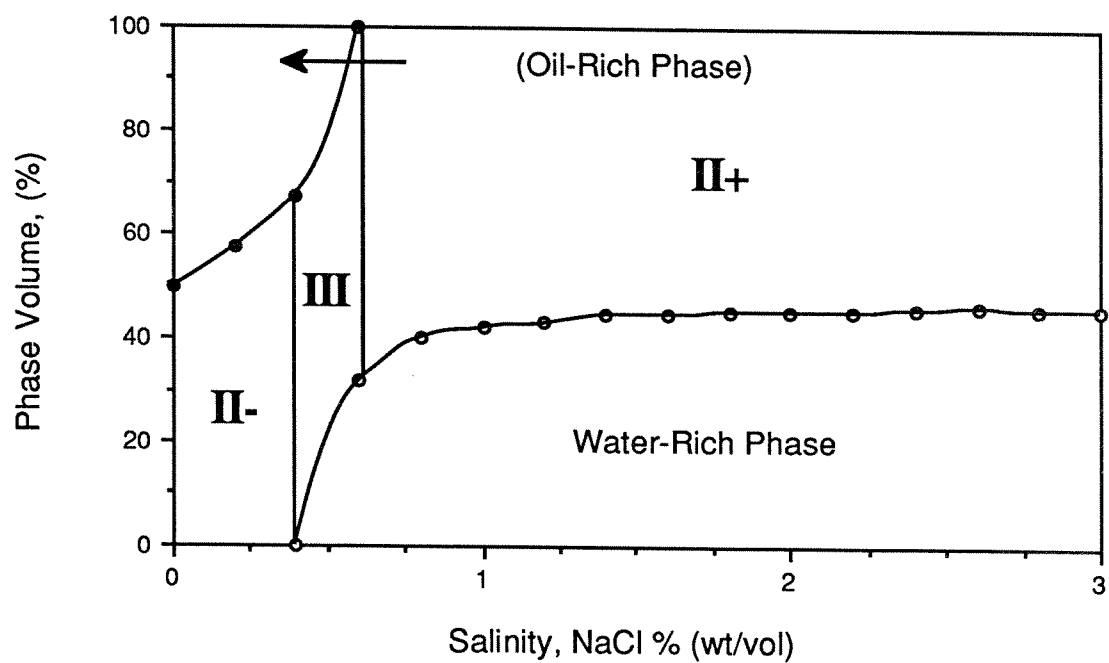


FIGURE A-2. - Phase behavior of 2% TRS 10-410, 1% T202, and 3% IBA with decane at 50°C.

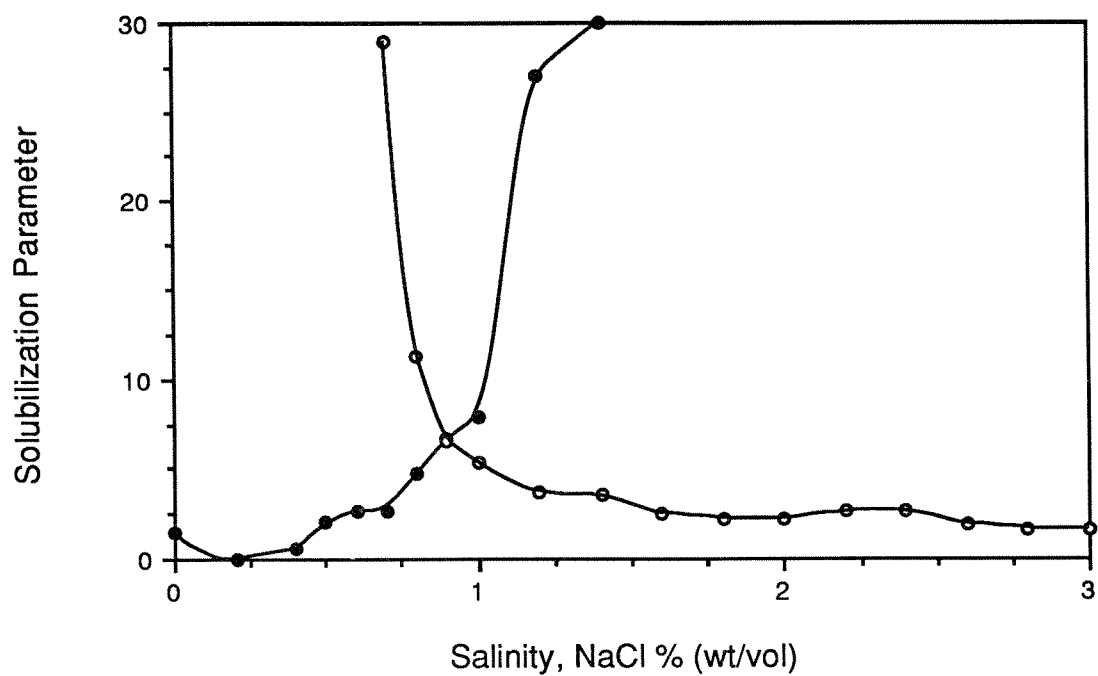
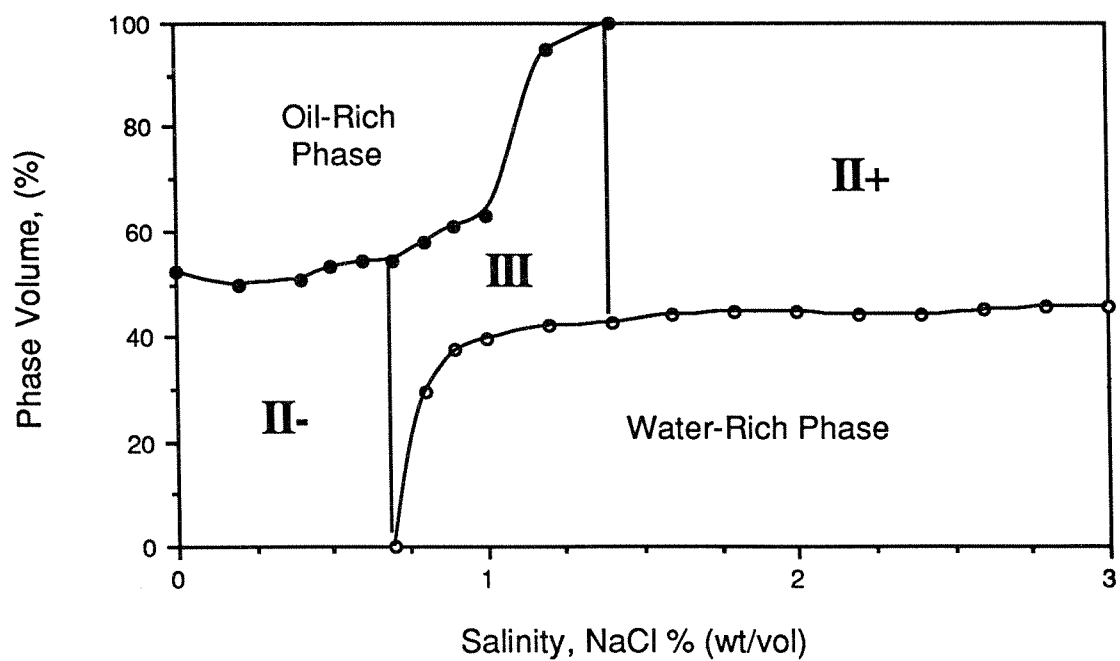


FIGURE A-3. - Phase behavior of 2.9% TRS10-410, 0.1% T202, and 3% IBA with decane at 50°C.

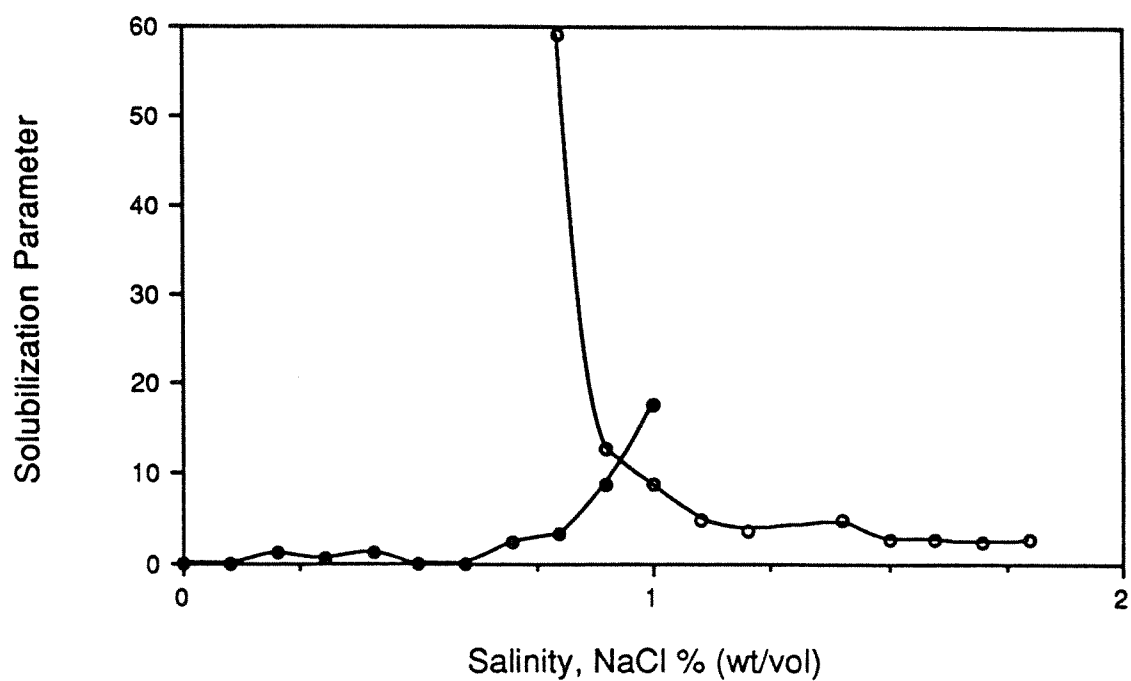
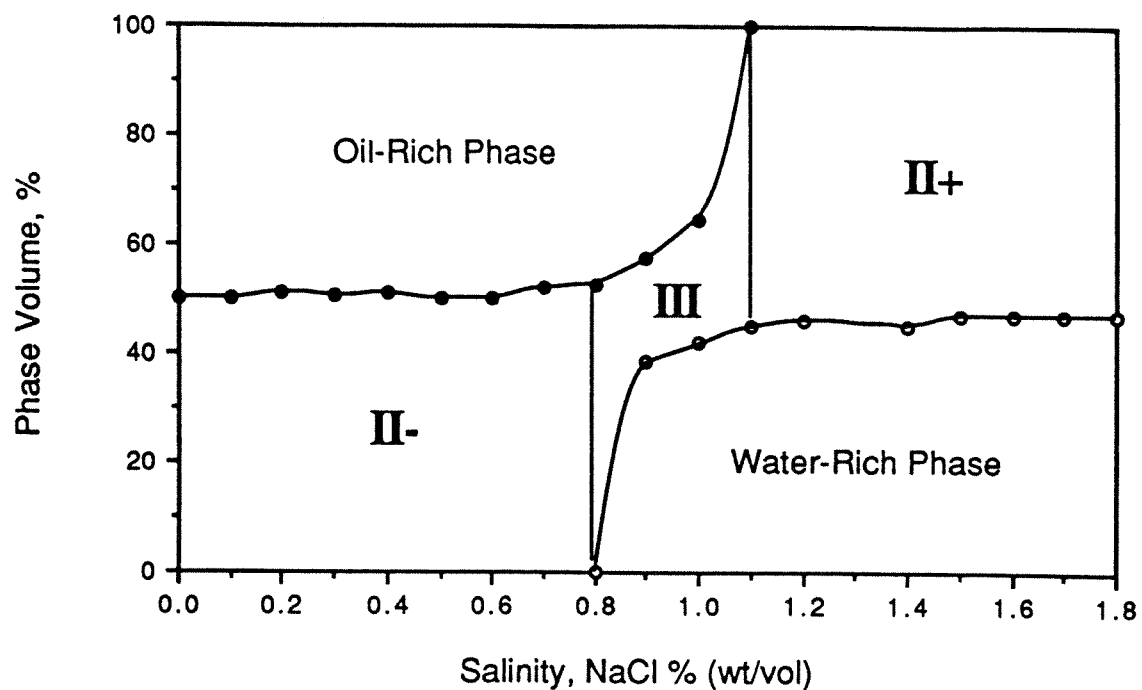


FIGURE A-4. - Phase behavior of 1.5% TRS 10-410 and 1.5% IBA with decane at 50°C.

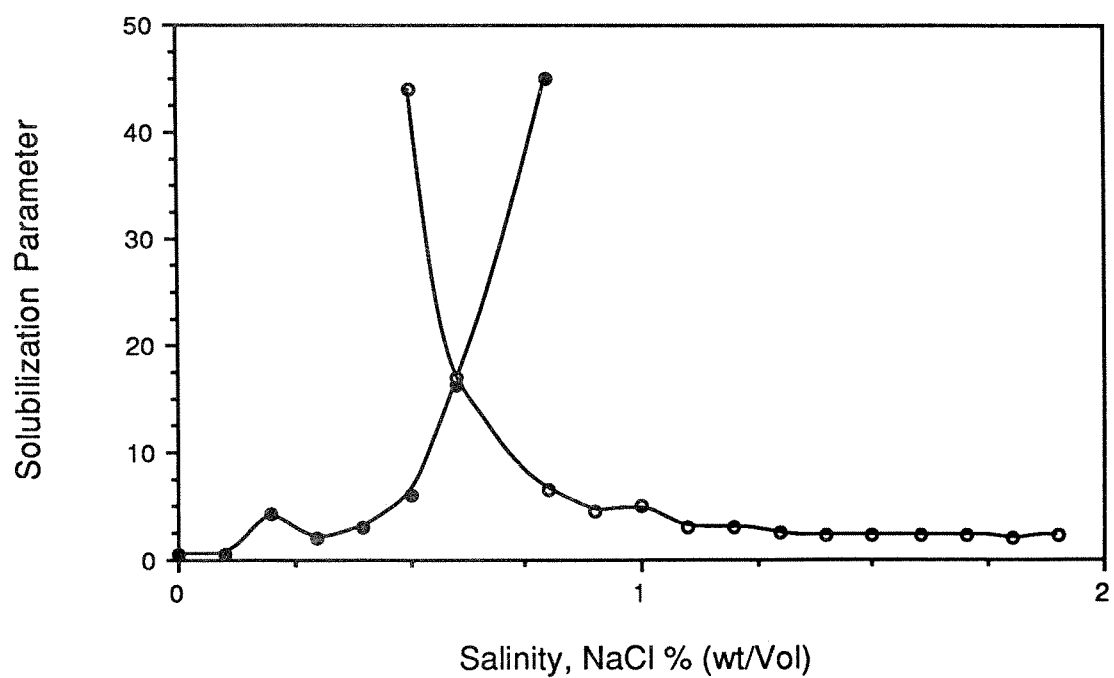
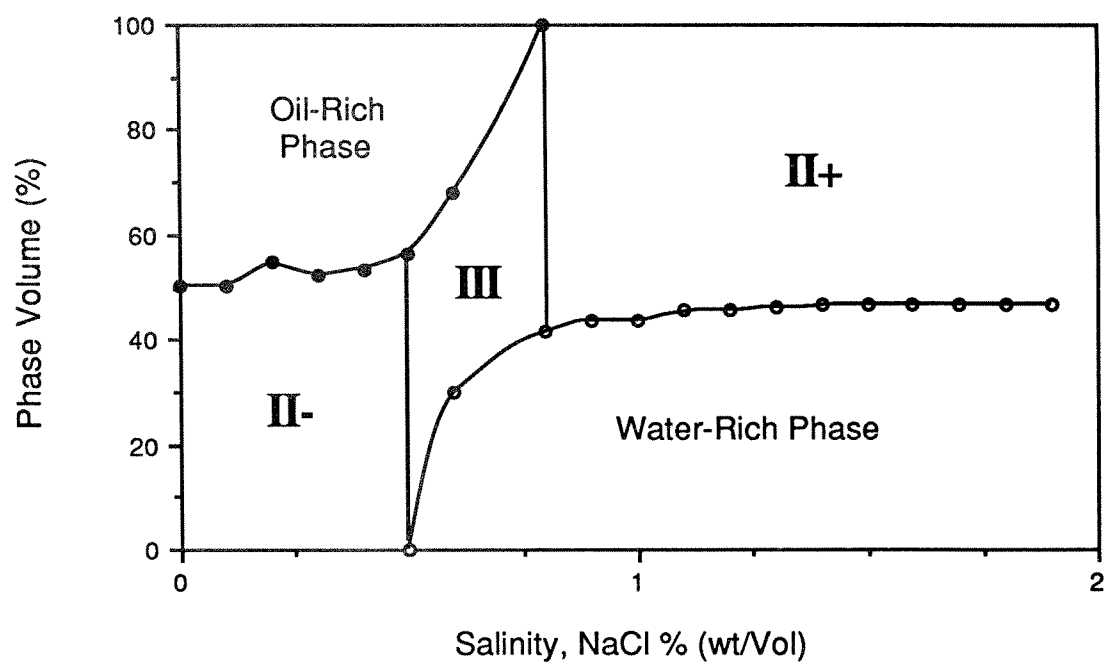


FIGURE A-5. - Phase behavior of 2% TRS10-410 and 3% IBA with decane at 50°C.

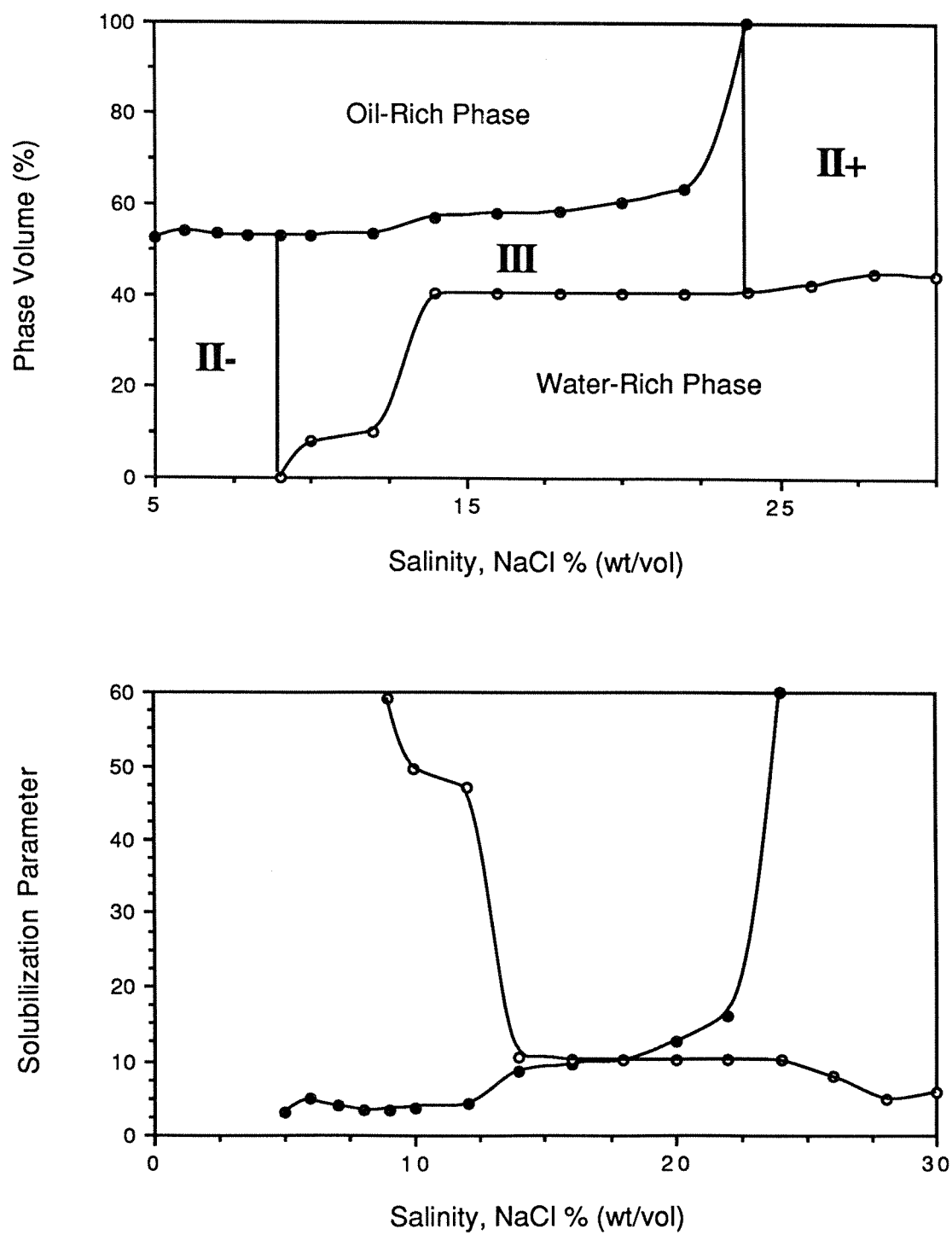


FIGURE A-6. - Phase behavior of 3% DMMC-W and 3% IAA with decane at 50°C.

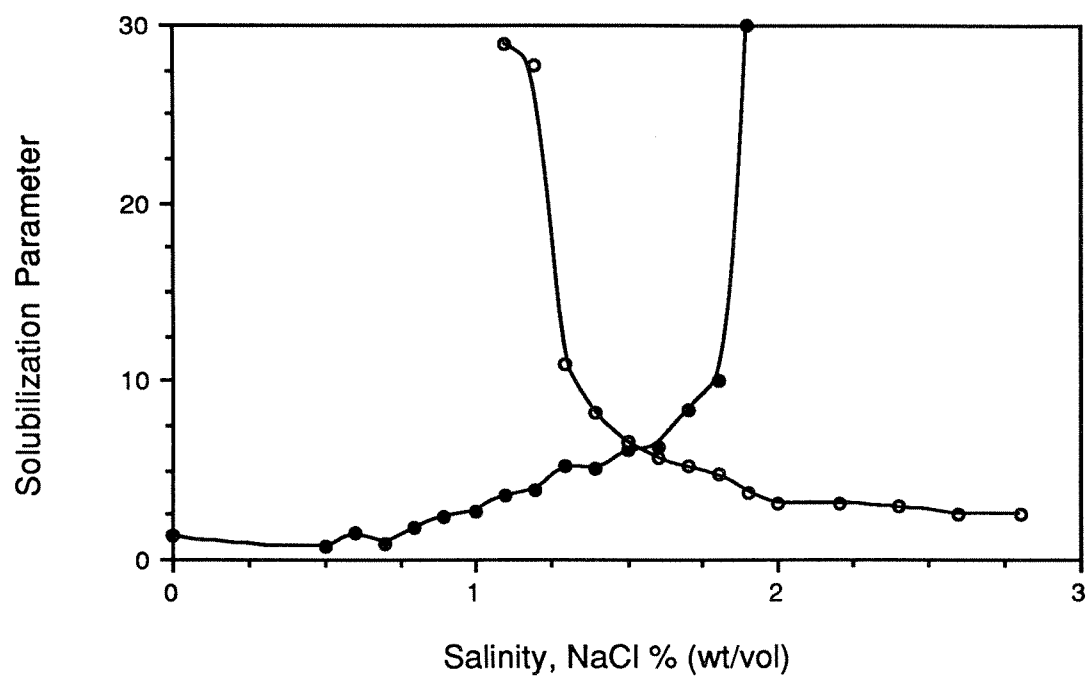
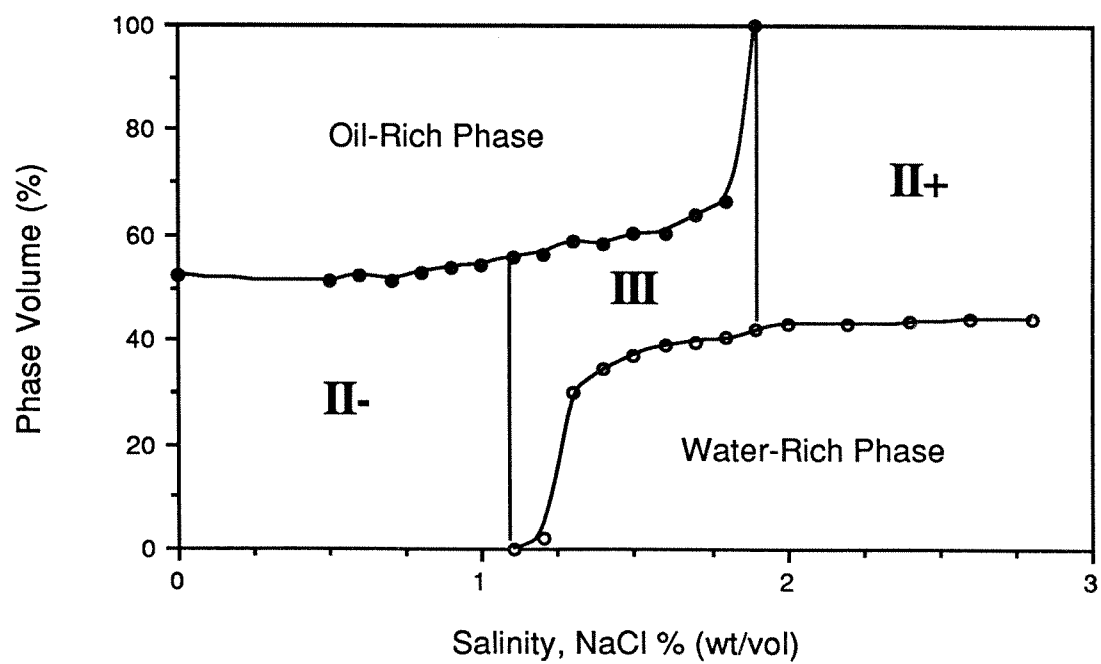


FIGURE A-7. - Phase behavior of 3% TRS 10-410 and 3% IBA with decane at 50°C.

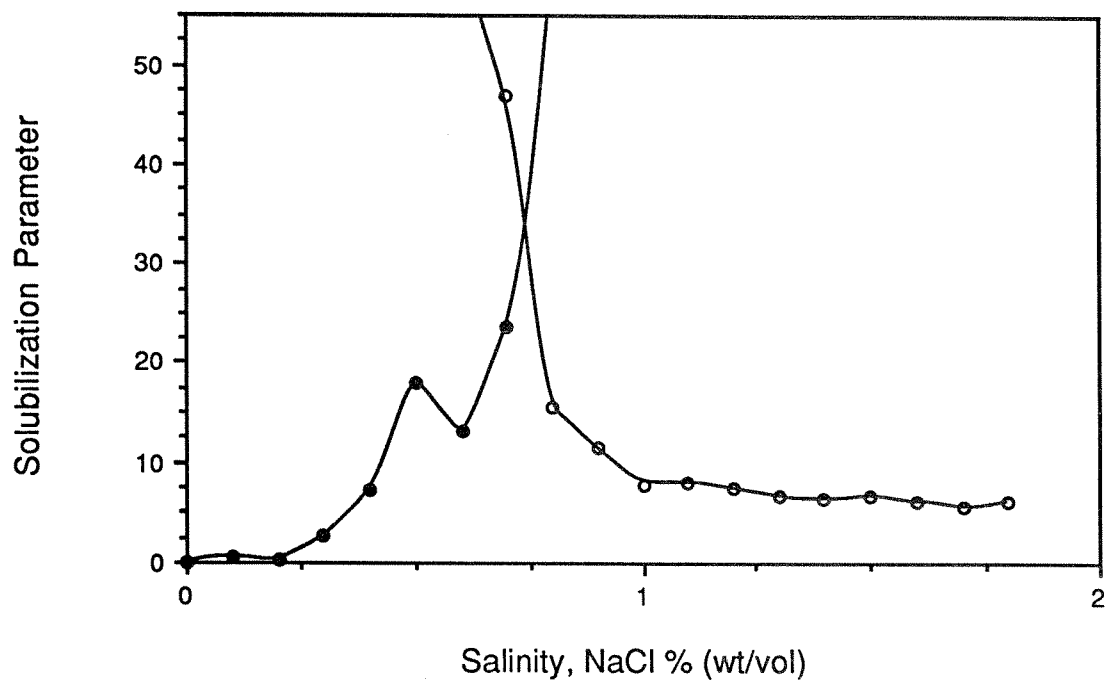
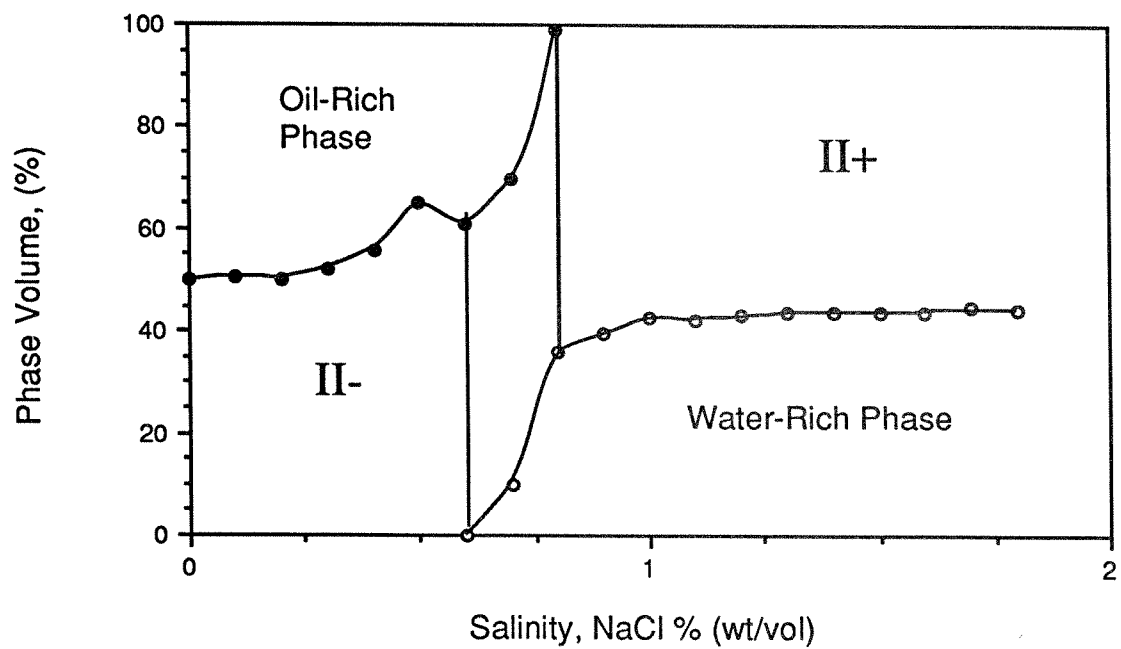


FIGURE A-8. - Phase behavior of 2.9% TRS10-410, 0.1% DM16-W, and 3% IBA with decane at 50°C.

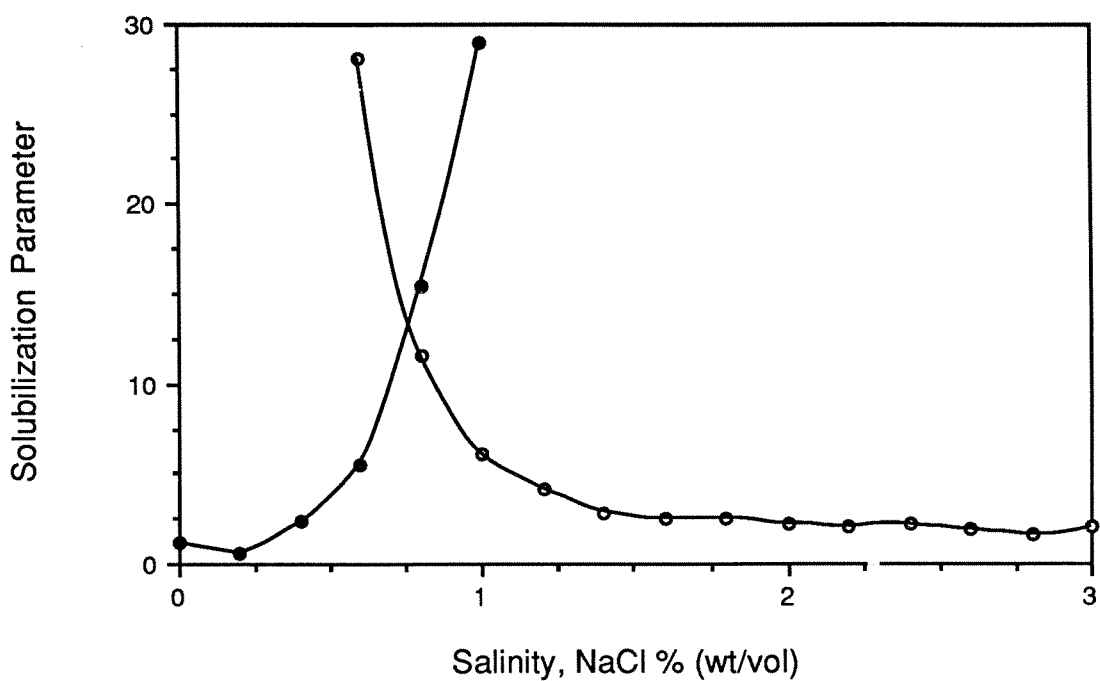
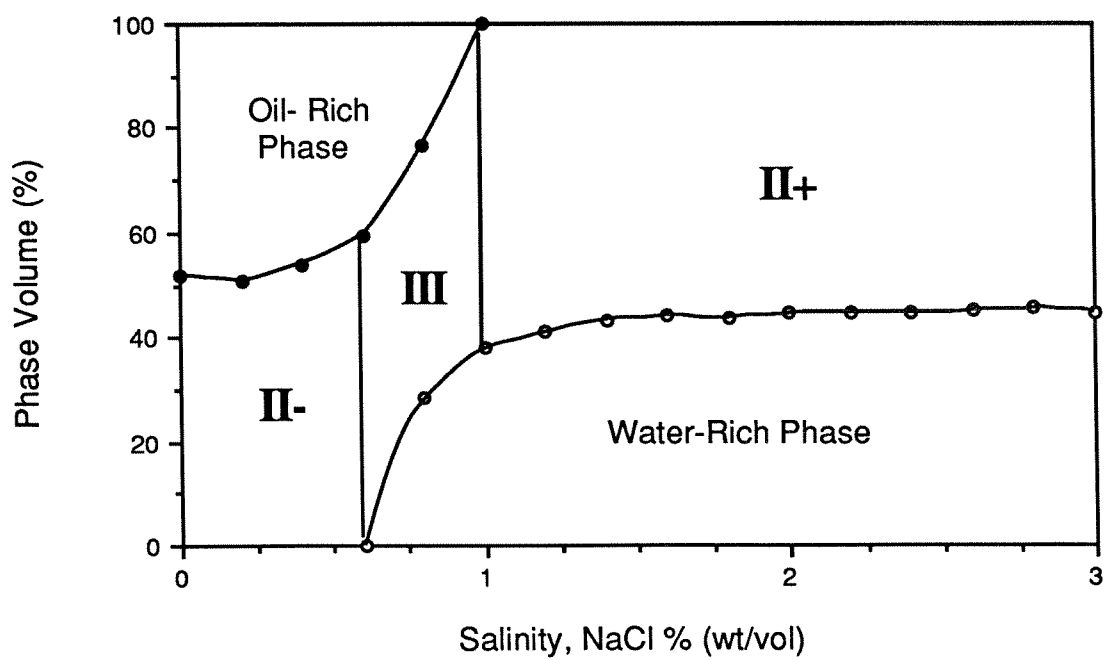


FIGURE A-9. - Phase behavior of 3% TRS 10-410, 0.1% T202, and 2.9% IBA with decane at 50°C.

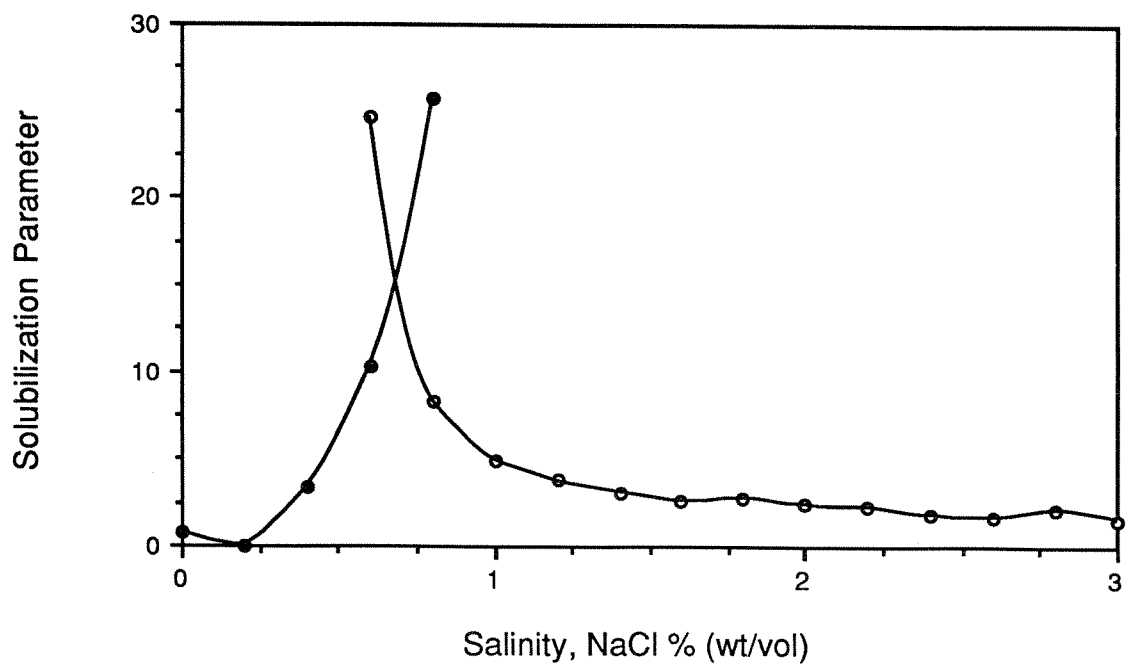
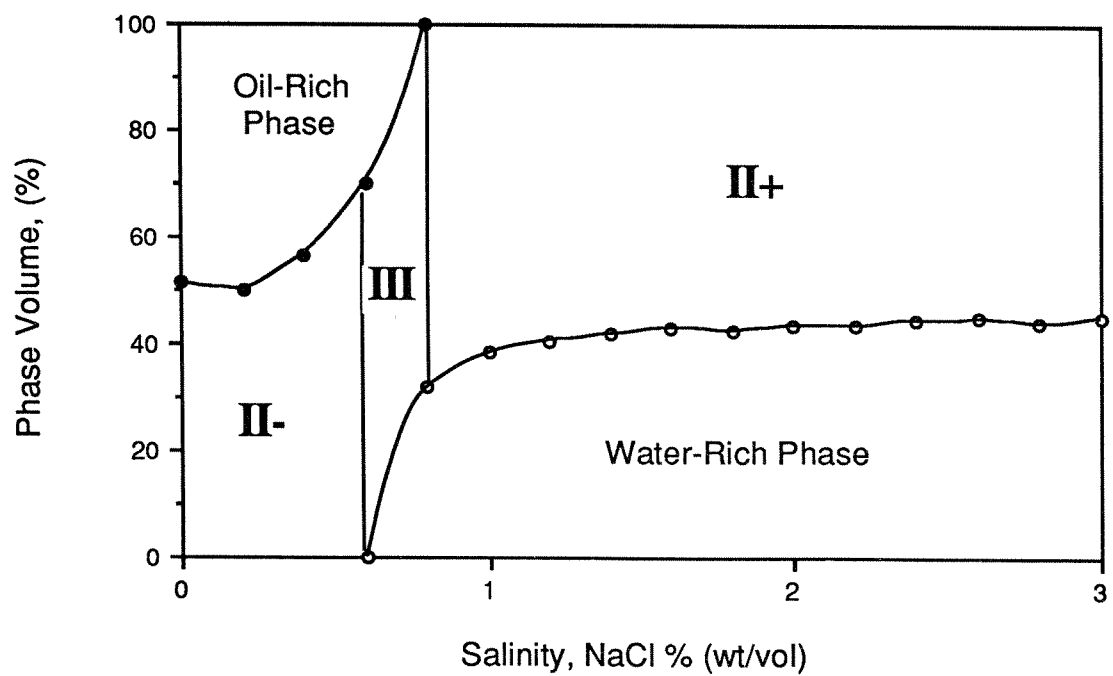


FIGURE A-10. - Phase behavior of 3% TRS 10-410, 0.5% T202, and 2.5% IBA with decane at 50°C.

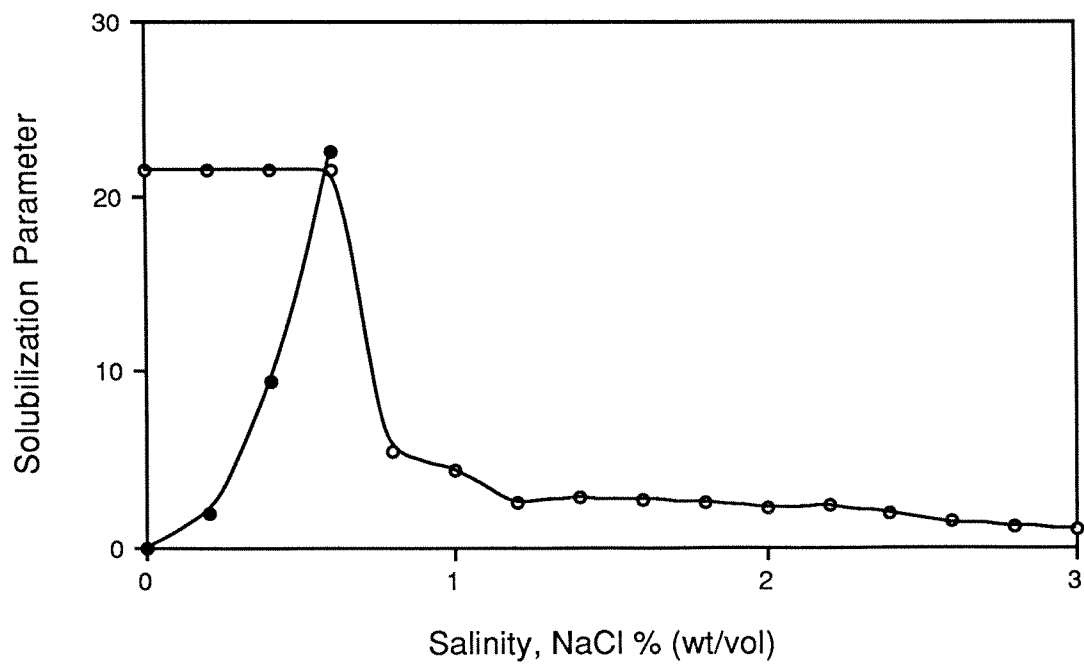
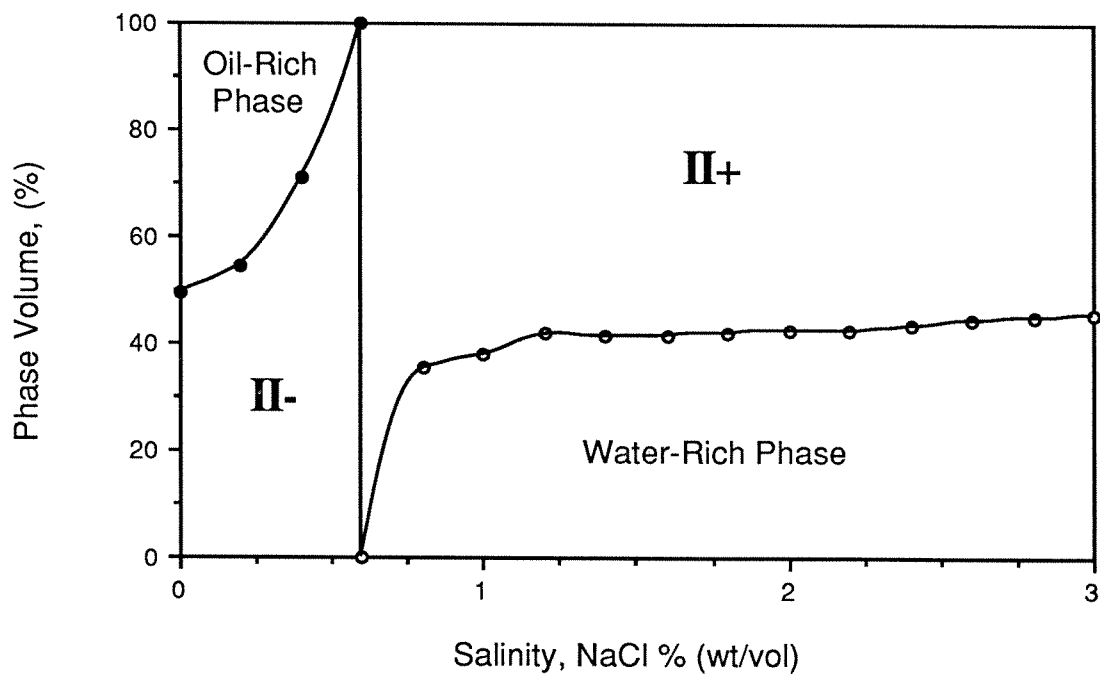


FIGURE A-11. - Phase behavior of 3% TRS10-410, 1% T202, and 2% IBA with decane at 50°C.

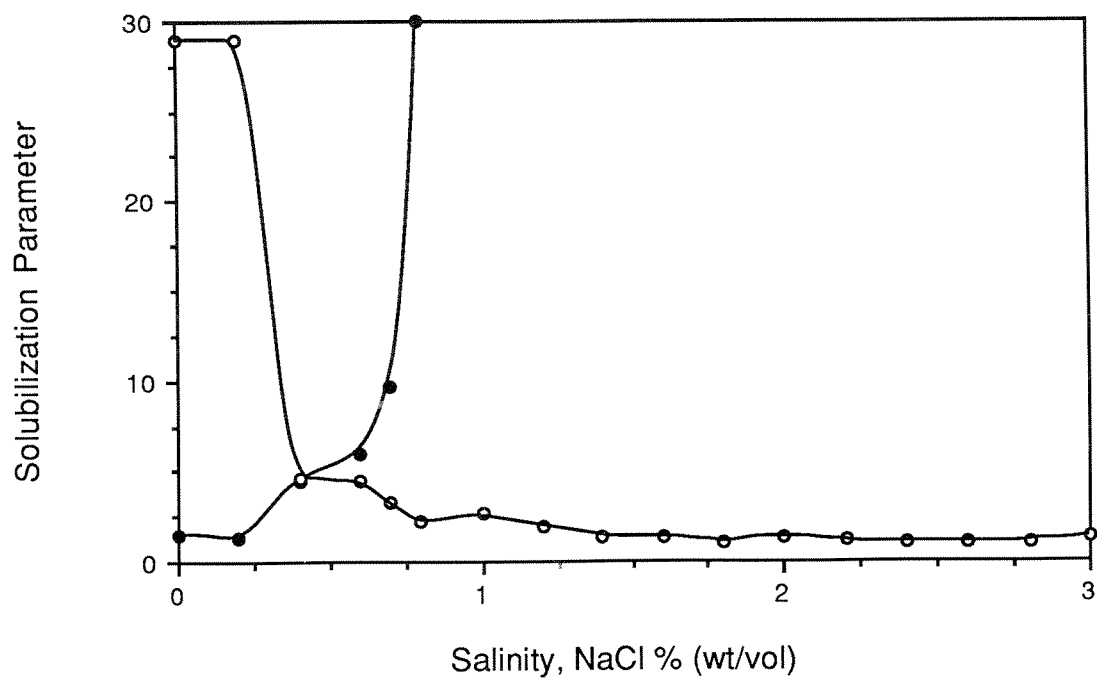
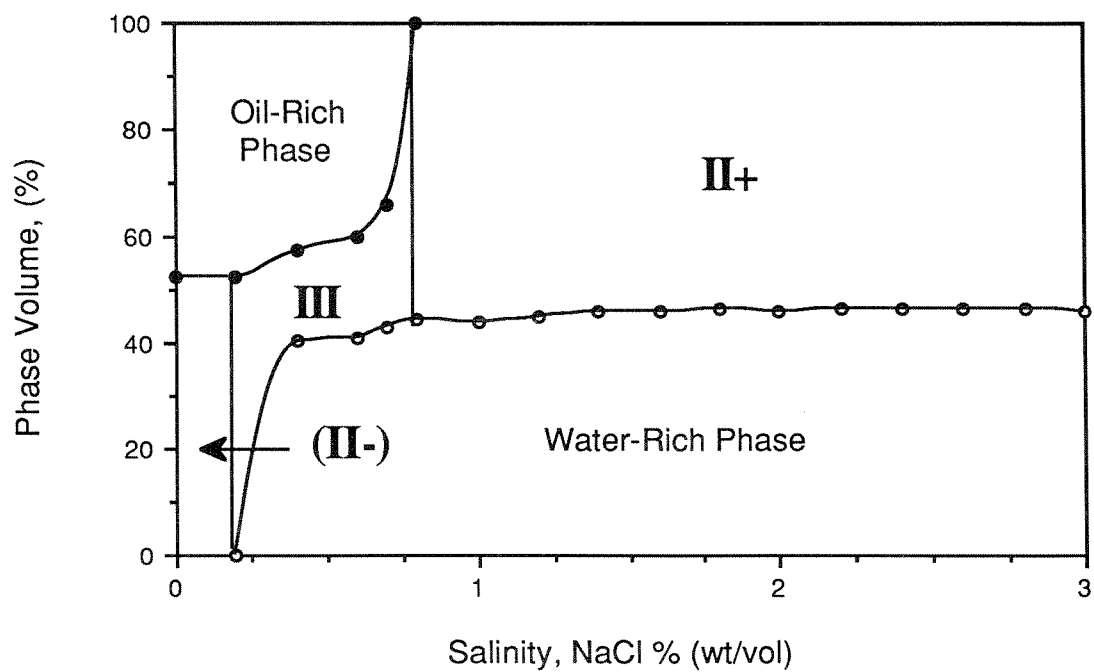


FIGURE A-12. - Phase behavior of 2.5% TRS 10-410, 0.5% T202, and 3% IBA with decane at 50°C.

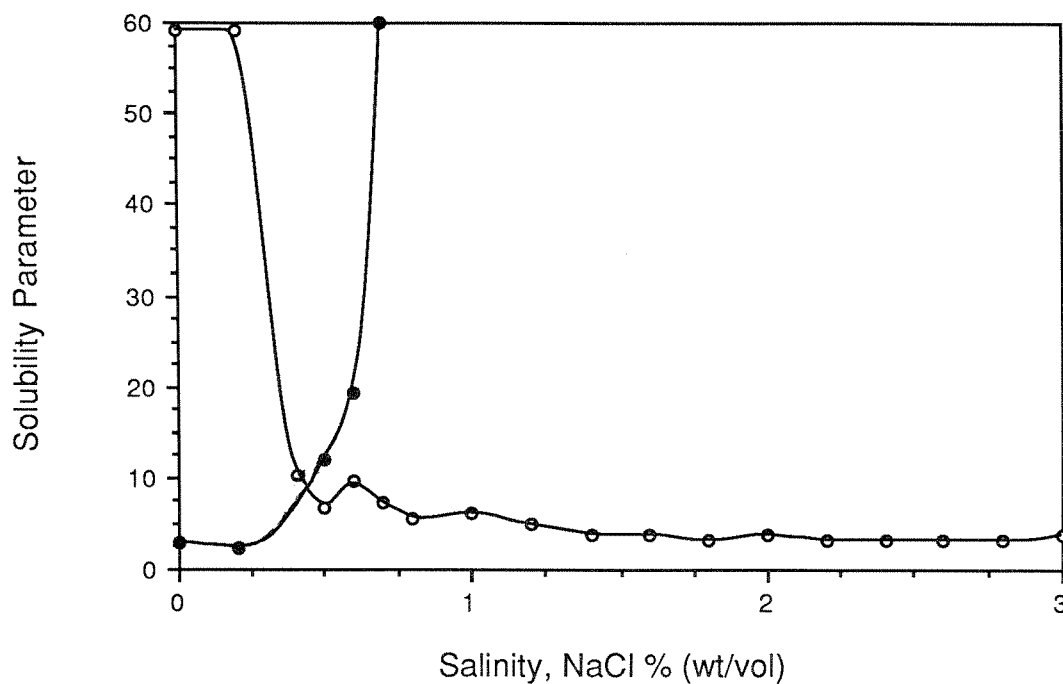
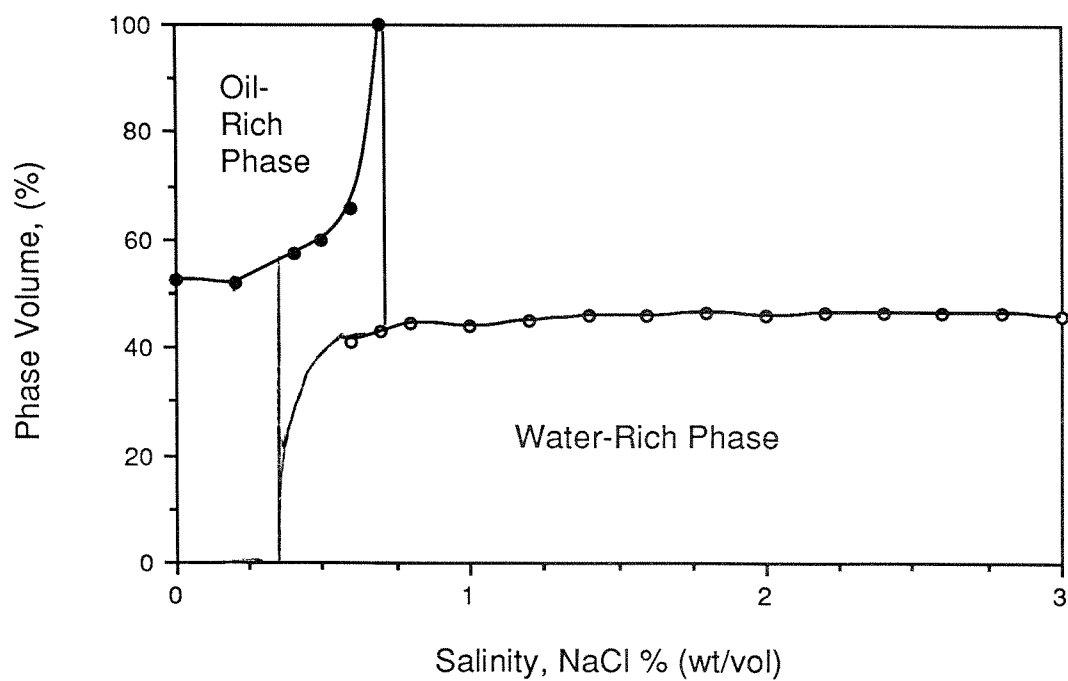


FIGURE A-13. - Phase behavior of 2.5% TRS 10-410, 0.5% T202, and 3% IBA with decane at 80°C.





